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INVESTIGATION OF ODOR CONTROL BY ALKALINE SODIUM HYPOCHLORITE
AND ALKALINE POTASSIUM PERMANGANATE SOLUTIONS

by

Reynold You-Jyh Chen

A Thesis
Submitted to the Faculty of Graduate Studies
Through the Department of
Chemical Engineering in Partial Fulfillment
of the Requirements for the Degree
of Master of Applied Science at
The University of Windsor

Windsor, Ontario, Canada

1978

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ABSTRACT

Odor control by wet scrubbing with alkaline sodium hypochlorite and alkaline potassium permanganate solutions was investigated. Butyraldehyde and n-butyl mercaptan were selected for tests in a 6-inch I. D. column packed with 2.3 feet of 5/8-inch stainless steel Pall rings. Odorant concentrations were determined by means of a gas chromatograph.

Solubilities of gaseous butyraldehyde and n-butyl mercaptan in pure water were measured at 0°, 25° and 40° C. Physical mass transfer data were obtained experimentally by scrubbing with water. The results indicate that the gas-side mass transfer resistance is negligible under the scrubbing conditions. Both reagents seem to give poor efficiencies for butyraldehyde removal, but can achieve very high removals of n-butyl mercaptan. The influence of oxidant and alkaline concentrations on the rate of absorption was also studied. With alkaline sodium hypochlorite solutions, an increase in the oxidant or alkaline concentrations has a positive effect on the enhancement factor for both butyraldehyde and n-butyl mercaptan. Similar effects on the enhancement factor for both odorous compounds were also found when scrubbing with alkaline potassium permanganate solutions.

Cost comparisons of these two reagents show that alkaline

potassium permanganate is slightly more economical for butyraldehyde removal, but alkaline sodium hypochlorite is much cheaper when scrubbing n-butyl mercaptan. The application of experimental data to packed bed scrubber design is also demonstrated.

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The author gratefully acknowledges Dr. G. P. Mathur, Dr. A. W. Gnyp, Dr. C. C. St. Pierre and Prof. M. B. Powley, for their guidance throughout this work, for their helpful discussions and suggestions on this thesis. Dr. S. J. W. Price kindly helped to check the measurement of odor concentrations with his total hydrocarbon analyzer.

Thanks also extend to Mr. George Ryan for his help in building the wet scrubbing system.

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I. INTRODUCTION

Odor control by wet scrubbing is possible over a wide range of gas flow rates, humidities, and odor concentrations. It is also useful for removing particulates accompanying odors in typical emissions. Cost comparisons of various odor control methods for rendering plants⁽¹⁾ and for spent grain dryers⁽²⁾ show that wet scrubbing is most economical and can be highly effective.

The selection of reagents for controlling various odorants has been studied by many investigators^(1,2,3,4,5). It may be concluded that there is no single practical reagent which can be used effectively and economically to control all the odor types encountered and, therefore, research on finding scrubbing mixtures which are highly effective and inexpensive is worthwhile. Among the many possible reagent combinations, it was found that alkaline sodium hypochlorite^(1,2,3) and alkaline potassium permanganate^(4,5) are two of the promising chemicals.

In designing a wet scrubbing unit, it is desirable to know the physico-chemical data and reaction kinetics related to the system. The objective of this research was to measure the mass transfer data and to investigate the effects of reagent and alkaline concentrations on the rates of absorption.

Industrial odors can be classified into three categories involving organic sulfur, organic nitrogen and carbonyl compounds.

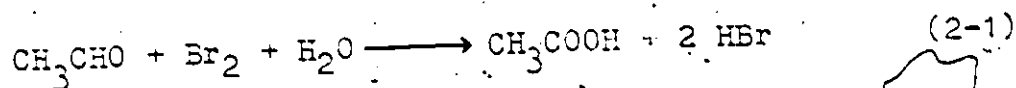
Most of organic nitrogen compounds are very soluble in water and hence may be easy to remove by simple water scrubbing. Consequently, this research is concerned with organic sulfur and carbonyl compounds which are only slightly soluble in water. Butyraldehyde and n-butyl mercaptan were selected as representative types of odors for this work.

II. LITERATURE REVIEW

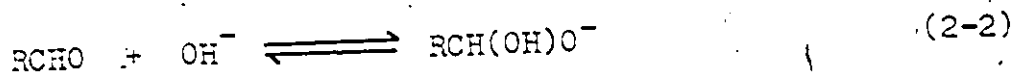
A. Chemical Reactions

1. Oxidation of Aldehydes

(6) Kaplan studied the oxidation of acetaldehyde by bromine in aqueous solutions over a pH range from 2 to 10. Aldehydes are oxidized to acids according to

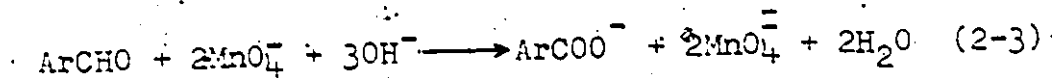


From the deuterium isotope effect and reaction kinetics it was concluded that aldehydes are oxidized via hydrates formed by processes of the type



Aldehyde hydrates are oxidized much faster than are the neutral molecules. The influence of pH on the oxidation of acetaldehyde by bromine water was studied further by Perlmutter-Hayman and Weissmann (7) who investigated the pH range from 1 to 7.5. At low pH (from 1 to 4) the influence is very slight. As the pH is increased beyond 5, the rate of oxidation rises due to the increased formation of aldehyde hydrates which are oxidized much more rapidly than the neutral aldehydes.

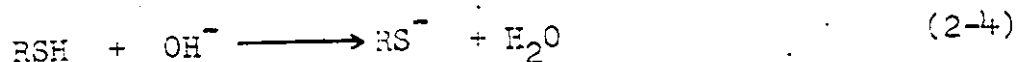
(3) Tomkins investigated the kinetics of oxidation of benzaldehyde by potassium permanganate. In alkaline solution, the following reaction is assumed to take place:



Aldehyde hydrates, similar to Kaplan's, were also suggested to be the intermediates in the oxidation of benzaldehyde. Benzaldehyde is oxidized much faster in the alkaline solution than in neutral solution. A more detailed study on the oxidation of benzaldehyde by potassium permanganate was carried out by Wiberg and Stewart⁽⁹⁾. The deuterium isotope effect was also studied and it was found that in a basic solution oxygen is not transferred from the permanganate but from the water. With an increase in pH, although the oxidative power of permanganate is retarded, the rate of oxidation is still increased due to the increased formation of aldehyde hydrates.

2. Oxidation of Mercaptans

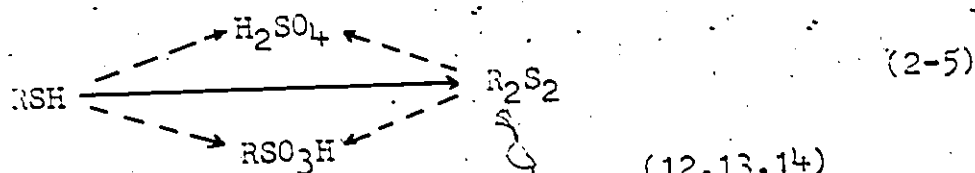
Mercaptans can dissolve into aqueous sodium hydroxide solution with the formation of mercaptides⁽¹⁰⁾ according to



The solubility of mercaptans in caustic solution is increased with increasing sodium hydroxide concentrations.

The action of sodium hypochlorite on mercaptans was studied by Birch and Morris⁽¹¹⁾. Mercaptans were oxidized by hypochlorite to sulfonic and sulfuric acids and disulfides.

A typical reaction can be illustrated by



There is only limited literatures (12,13,14) concerning (12) the oxidation of mercaptans by potassium permanganate. Reychler prepared hexadecanesulfonic acid by warming hexadecyl mercaptan with potassium permanganate. A small amount of dihexadecyl sulfone was found as a byproduct in this reaction (13)

B. Odor Removal by Wet Scrubbing with Chemical Reaction (15)

Posselt and Reidies studied odor abatement with potassium permanganate solutions. Odorants included amines, phenols and organic sulfur compounds. The experimental tests were carried out in gas washing bottles. Odor levels were evaluated by the ASTM Syringe Method D 1397-52. Their results indicated that potassium permanganate can be applied to a wide variety of odorous compounds. Only triethylamine, acetaldehyde and m-chlorophenol showed poor removal efficiencies.

(5) Anderson and Adolf evaluated the effectiveness of potassium permanganate for the control of odorous emissions from rendering and food processing industries. Aldehydes, ketones, alcohols, organic acids, organic nitrogen compounds

and organic sulfur compounds were tested in gas wash bottles. Solutions of 2 % potassium permanganate at pH 9 (2 % borax), pH 11 (2 % Na_2CO_3) and pH 12 (adjusted with NaOH) were utilized as scrubbing liquids. Odor levels and odorant concentrations were determined with the syringe technique, ASTM Method D 1359-57, and gas chromatography respectively. It was found that odor reductions ranging from 30 to 98 % could be achieved. The effect of scrubbing solution pH on odor removal was also studied. An increase in the pH of KMnO_4 solutions had a positive effect on the odor removal efficiency.

(16)
High and Li Puma conducted a pilot study to evaluate scrubbing solutions for controlling animal rendering plant odors. Their pilot plant scrubber was a 5,000 scfm Zurn Air System's "Dustractor" operating at pressure drops ranging from 5 to 10 inches of water. Water, calcium hypochlorite, chlorine gas, hydrogen peroxide, lime, politol "S", soda ash, potassium permanganate, sodium bisulfite and matasilicate were tested for their effectiveness of odor removal. The experimental results indicated that calcium hypochlorite solution was the most effective odor reducing agent under the test conditions.

(2)
First, Gowan and Quinby conducted pilot plant studies on spent grain dryer offgas cleaning. A four-stage reactor-absorber in which each stage had a 12" * 15" cross section, was used for this test program. The offgas was treated with

different dosages of chlorine ranging from 2 to 9 ppm and then scrubbed with 20 % NaOH solution. Odorant concentrations were determined with a gas chromatograph. The odor removal efficiency increased with increasing chlorine concentrations up to 5.7 ppm. When the chlorine exceeded 5.7 ppm, it was found that odor removal no longer increased. Instead a distinct hypochlorite odor was detected. A full scale scrubber has performed exactly as pilot test data predicted.

A detailed investigation of reagents for rendering plant odor control was carried out by Doty et. al. ⁽¹⁾. They used both a bubbler and a packed bed scrubber to test the odor removal efficiencies of various reagents. The gas chromatographic method was used to determine odor concentrations. The results of bubbler scrubber tests showed that the most effective reagents are the strong oxidizers: sodium hypochlorite, potassium permanganate and sodium persulphate. The tests with the packed scrubber involved a 6" ID * 2'-0" high bed packed with $\frac{1}{2}$ " Intalox saddles. Results of the packed bed scrubber studies are summarized in Table 2-1. Hypochlorite seems to be the most effective of all reagents tested. Permanganate reacted more slowly but attacked some odorants not handled by hypochlorite. A further study to confirm these findings with actual rendering plant emissions was conducted by Snow and Huff ⁽³⁾. A three-stage laboratory scale packed bed scrubber, similar to Doty's

Odor Removal, %									
Odorant Reagent	Valer- aldehyde	Dipropyl Sulfide	Amyl Alcohol	Trimethyl- Amine	Butyric Acid	Butane- dione	Tert- Butyl Amine	Hepta- diene	Dimethyl Disulfide
Water	30	0	80-90	80-90			>90	0	10
NaOCl, 1 %	10	>90	80	>90				20	50
H ₂ O ₂ , 3 %	>90	0	75				>90	0	slight
Potassium Permanganate 3 %	30	10-25	40-80	>90				25	20-75
Sodium Bisulfite 5 %	>90	10	75						
HCl, 5 %	0	0	80	>90					
Sodium Hydroxide 5 %	10-30	0	0-60	0	>90	>90	>90		

Table 2-1. Summary of Tests of Packed Bed Scrubber

(1)

unit, and a full scale horizontal spray scrubber were designed and installed at the rendering plant site. These two devices were used to evaluate different scrubbing combinations and to determine the effect of various conditions on performance. Odor concentrations were measured by odor panels and a gas chromatograph. Their results showed that the multiple stage absorption with alkaline sodium hypochlorite was the most effective scrubbing combination. They suggested that maintaining the pH above 11, preferably above 12, is important.

A systematic investigation of the selection of reagents for various types of odorants was made by Murthy⁽¹⁷⁾. Industrial odor emissions were classified into sulfurous compounds (mercaptans and sulfides), nitrogenous compounds (ammonia and amines) and oxygenated hydrocarbons (aldehydes and ketones). These three types of odorants were tested in a bench-scale semi-batch bubbler scrubber. Odor concentrations were determined by means of gas chromatography. The results indicated that

- i. sodium hydroxide is a promising reagent for removing mercaptans;
 - ii. sulfuric acid, sulfamic acid and hydrochloric acid are the most effective reagents for amines; and
 - iii. sodium bisulfite is the best reagent for aldehyde removal.
- The effect of reagent concentrations on odor removal efficiency was studied over the 1 to 5 % by weight range as shown in

Figure 2-1. Both permanganate and hypochlorite showed a positive effect on the rate of absorption. The effect of the pH of permanganate solutions was also studied over the pH range from 3 to 10. The results are shown in Figure 2-2. It was found that an increase in the pH of permanganate solutions increased the removal efficiency of amines and mercaptans but had a negative effect on the removal of aldehydes.

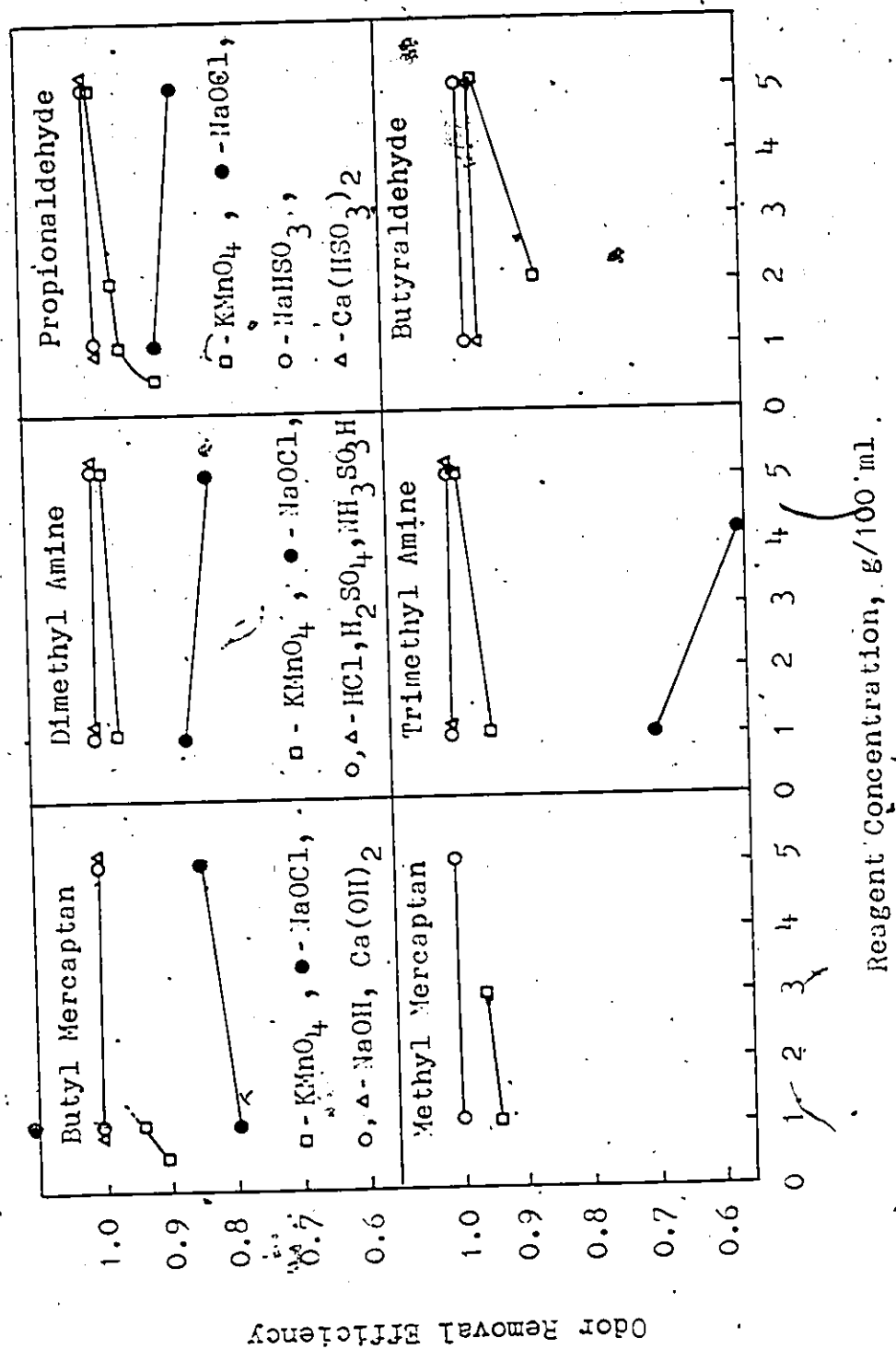


Figure 2-1. Effect of Reagent Concentration on Odor Removal (17)

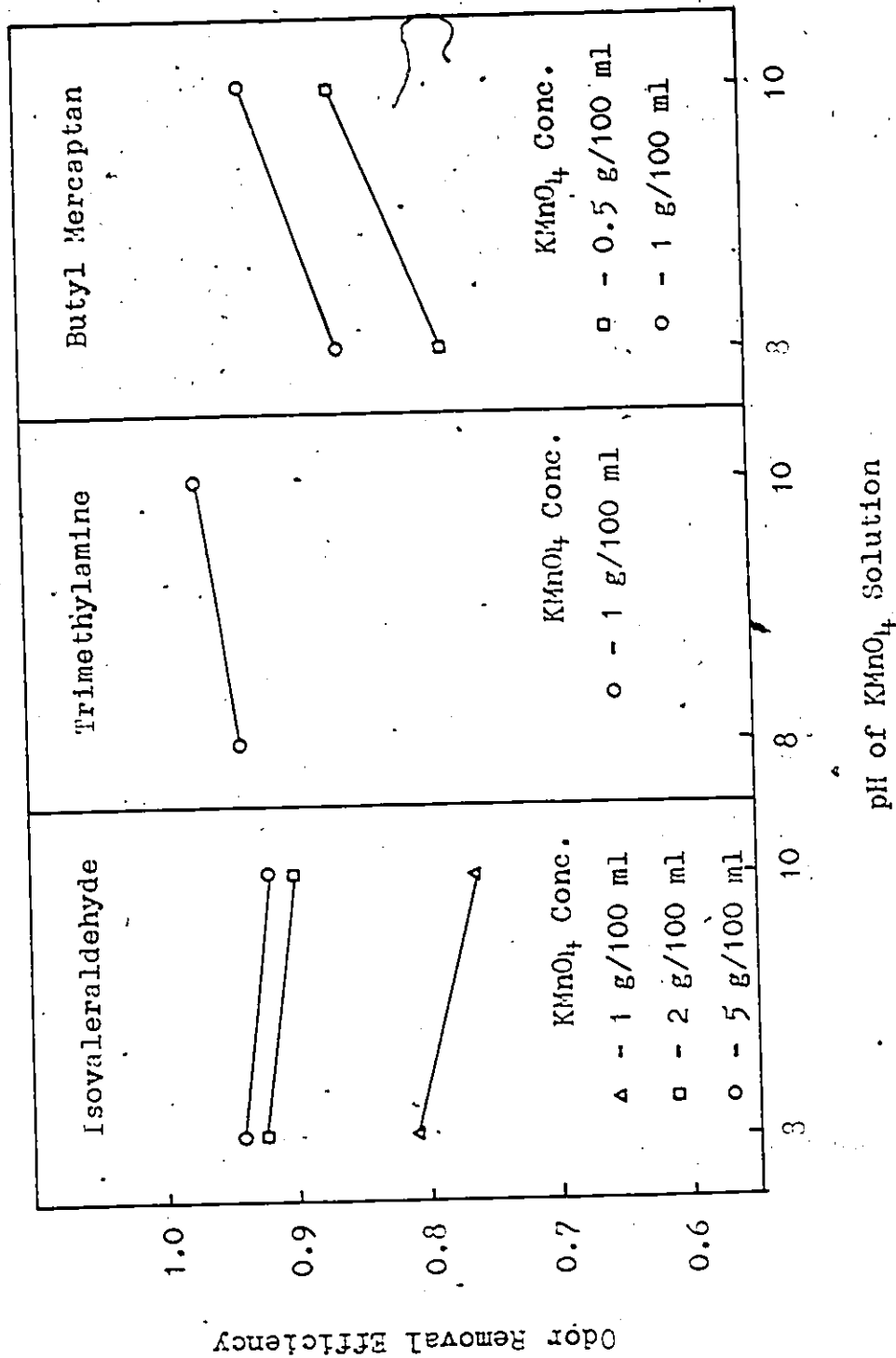


Figure 2-2. Effect of Permanganate Solution pH on Odor Removal (17)

III. GENERAL THEORY

A. Solubility of a Gas in a Liquid

In most cases of wet scrubbing, as long as the concentration of the dissolved gas is low and the temperature and pressure are not too low or too high respectively, Henry's law can be applied. Then the equilibrium relationship between the partial pressure of the solute in the gas phase and its concentration in the liquid phase can be expressed by the linear relationship

$$p = H_e' \cdot x \quad (3-1)$$

where

p = Partial pressure of solute in gas, mm Hg

H_e' = Henry's law constant, mm Hg/mole fraction

x = Mole fraction of solute in liquid

A common alternate form of Henry's law constant is defined in units of mole fraction in the gas phase / mole fraction in the liquid phase, from

$$y = H_e x \quad (3-2)$$

where

y = Mole fraction of solute in gas

H_e = Henry's law constant, mole fraction/mole fraction

The Henry's law constant for a gas in water can be established experimentally. However, if the gas dissolution is accompanied with chemical reaction, it is not possible to measure the Henry's law constant by the conventional methods. From theoretical considerations, it may be possible to infer the solubility of a gas in solutions with which it reacts from the solubility of the gas in neutral solutions. It has been found that solubilities of gases in non-reacting electrolyte solutions can be estimated to within 10 % from the expression (13)

$$\log(H_e/H_e^0) = hI \quad (3-3)$$

where H_e^0 is the value in water and I is ionic strength of the solution defined by

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (3-4)$$

C_i being the concentration of ions of valency Z_i . The parameter h is the sum of constants which are characteristic of cations, anions and gases as given by

$$h = h_c + h_a + h_g \quad (3-5)$$

The contributions of various gases and ions to the parameter h are summarized in Table 3-1 (19,20,21).

In mixed electrolytes it was suggested that the value of H_e will given by an expression of the form

Gas	Temp °C	h_g	Gas	Temp °C	h_g	Cation	h_c	Anion	h_a
CO ₂	25	-0.2277	CO ₂	0	-0.2110	Li ⁺	-0.0416	Cl ⁻	0.3416
N ₂	25	-0.1904		15	-0.2222	Na ⁺	-0.0183	Br ⁻	0.3310
O ₂	25	-0.1892		40	-0.2327	K ⁺	-0.0362	I ⁻	0.3124
H ₂	25	-0.2115	O ₂	0	-0.1653	Cs ⁺	-0.0584	SO ₄ ⁻²	0.3446
N ₂ O	25	-0.2141		15	-0.1786	Mg ⁺²	-0.0568	NO ₃ ⁻	0.3230
C ₂ H ₂	25	-0.2240		20	-0.1771	Ca ⁺²	-0.0547	CO ₃ ⁻²	0.3754
H ₂ S	25	-0.2551	H ₂	5	-0.2106	Ba ⁺²	-0.0473	OH ⁻	0.3875
SO ₂	25	-0.3154		10	-0.2170	Al ⁺³	-0.0726	CNS ⁻	0.2612
NH ₃	25	-0.2394		15	-0.2197	NH ₄ ⁺	-0.0737	PO ₄ ⁻²	0.3265
C ₂ H ₄	25	-0.1951		20	-0.2132	H ⁺	-0.1110	SO ₃ ⁻²	0.3275
He	25	-0.2220	C ₂ H ₂	15	-0.2124	Rb ⁺	-0.0449	HSO ₃ ⁻	0.3869
Ne	25	-0.2240	SO ₂	35	-0.3112	Cd ⁺²	-0.0062	HS ⁻	0.3718
Ar	25	-0.1866	C ₂ H ₄	15	-0.2003	Zn ⁺²	-0.0590	ClO ₂ ⁻	0.3497
Kr	25	-0.1762				Sr ⁺²	-0.0445	MnO ₄ ⁻	0.3321
N ₂ O	5	-0.2143				Fe ⁺²	-0.0602		
	10	-0.2156				Co ⁺²	-0.0534		
	15	-0.2118				Ni ⁺²	-0.0520		
	20	-0.2128				Cr ⁺³	-0.0986		
	40	-0.2179				Mn ⁺²	-0.0625		

Table 3-1. The Contribution to h by Various Gases and Ions (19,20,21)

$$\log(H_e/H_e^\circ) = \sum h_i I_i \quad (3-6)$$

where I_i is the ionic strength attributable to species i electrolyte and h_i has the value characteristic of that electrolyte.

B. Absorption Theory

1. Diffusion Model

According to the two film model, there is a stagnant layer on both the gas and liquid sides of the interface as shown in Figure 3-1. The gaseous odorant must diffuse through the other gas (usually insoluble) to reach the interface. Consequently, the concentration of the odorant at the interface is lower than in the bulk gas. At the interface, the gaseous odorant dissolves into the liquid to an extent depending on the solubility of the gas in the liquid. In the film on the liquid side, the dissolved odorant will diffuse from the interface to the bulk of the liquid. There is no convection in the films. The gaseous odorant moves from the bulk gas to the bulk liquid by molecular diffusion only.

In the steady state, the mass transfer flux can be expressed in terms of mass transfer coefficients and driving forces for each phase, according to

$$N = k_g' (p - p_i) = k_l' (A_i - A) \quad (3-7)$$

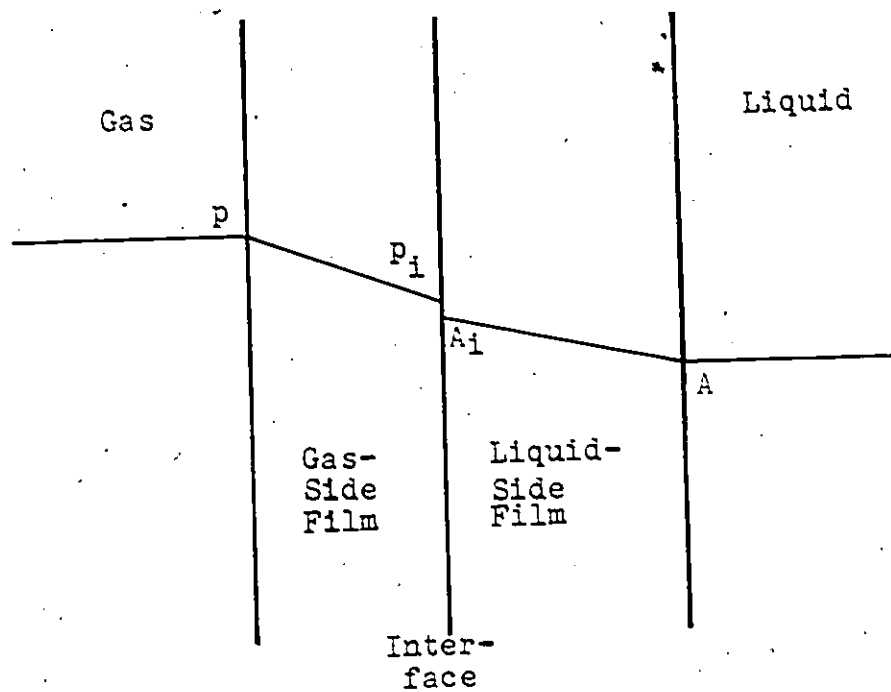


Figure 3-1. Two Film Diffusion Model

where

N = Mass transfer flux of solute, lb mole/(ft²)(hr)

k_g = Gas-side mass transfer coefficient, lb mole/(ft²)(hr)(atm)

p = Partial pressure of solute in gas, atm

p_i = Partial pressure of solute at the interface, atm

k_l = Liquid-side mass transfer coefficient, ft/hr

A = Concentration of absorbed gas in liquid, lb mole/ft³

A_i = Concentration of absorbed gas in liquid at the interface, lb mole/ft³

Equation 3-7 is generally expressed in terms of mole fractions of solute as given by

$$N = k_g (y - y_i) = k_l (x_i - x) \quad (3-8)$$

where

k_g = Gas-side mass transfer coefficient, lb mole/(ft²)(hr)

y = Mole fraction of solute in bulk gas

y_i = Mole fraction of solute in gas at the interface

k_l = Liquid-side mass transfer coefficient, lb mole/(ft²)(hr)

x = Mole fraction of absorbed gas in bulk liquid

x_i = Mole fraction of absorbed gas in liquid at the interface

It is not possible to measure the mole fraction of the solute in the gas or liquid at the interface. Therefore, it is common to employ overall mass transfer coefficients based on

overall driving forces. On the basis of overall driving forces the rate of absorption of odorant from the gas phase can be expressed in terms of

$$N = K_G (Y - y^*) = K_L (x^* - x) \quad (3-9)$$

where K_G and K_L are the overall mass transfer coefficients in the gas film and in the liquid film and are given by

$$1/K_G = 1/k_g + H_e/k_l \quad (3-10)$$

$$1/K_L = 1/k_l + 1/(k_g H_e) \quad (3-11)$$

y^* is the mole fraction of solute in the gas in equilibrium with x , and x^* is the mole fraction of the dissolved solute in equilibrium with y , y^* and x^* can be expressed by the equations

$$y^* = H_e x \quad (3-12)$$

$$x^* = y / H_e \quad (3-13)$$

2. Wet Scrubbing Without Chemical Reaction or With a Very Slow Reaction

When the rate of reaction is zero or negligibly small, a material balance on the odorant in the countercurrent wet scrubber shown in Figure 3-2, gives

$$-d(G_m y) = N a dz = -G_m dy - y dG_m \quad (3-14)$$

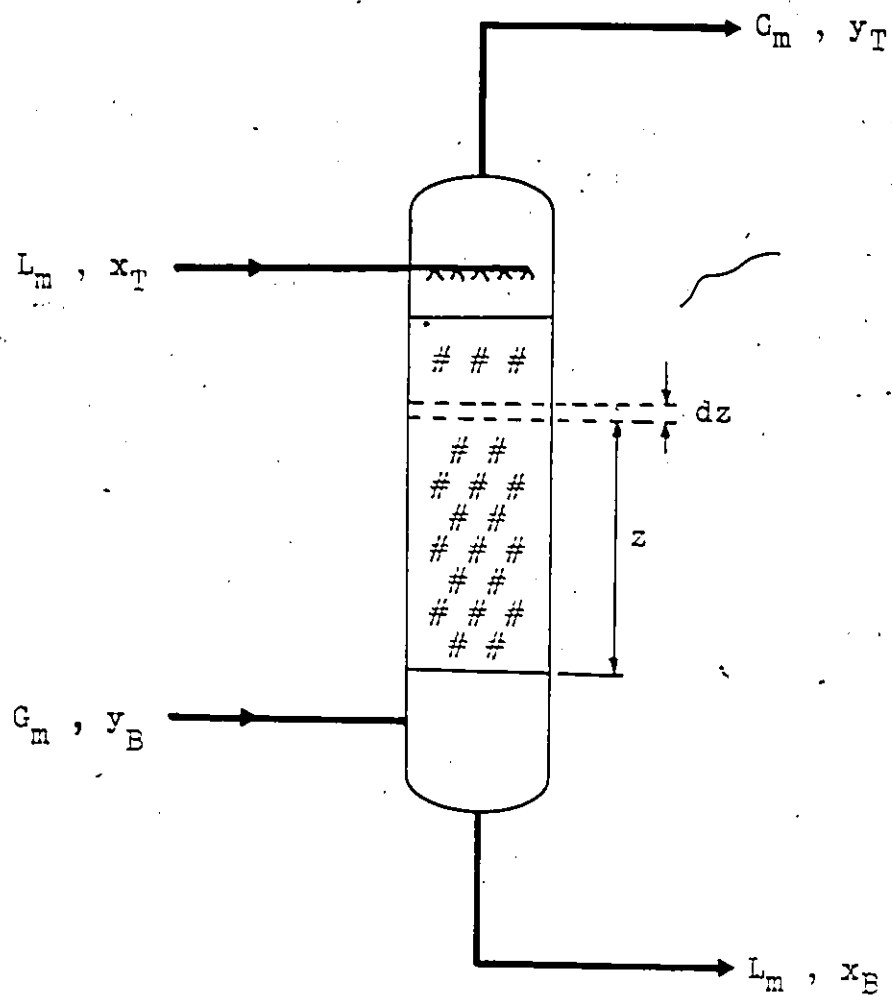


Figure 3-2. Packed Tower

where

- G_m = Gas molar flux, lb mole/(ft²)(hr)
- y = Mole fraction of solute in gas
- N = Mass transfer flux of solute, lb mole/(ft²)(hr)
- a = Interfacial area per unit of packed volume, ft⁻¹
- z = Height of packed bed

If only a single pure component is involved in the system

$$dG_m = - N a dz \quad (3-15)$$

Combining Equations 3-14 and 3-15 gives

$$N a dz = - \frac{G_m dy}{(1 - y)} \quad (3-16)$$

Substituting Equation 3-9 into Equation 3-16 yields

$$K_G a dz = - \frac{G_m dy}{(1 - y)(y - y^*)} \quad (3-17)$$

For a dilute system in which Henry's law is obeyed, the integral of Equation 3-17 can be expressed by the algebraic function developed by Colburn (22)

$$K_G a = \frac{G_m}{Z(1 - S)} \ln[(1 - S)(y_B/y_T) + S] \quad (3-18)$$

where

$$S = H_e G_m / L_m \quad (3-19)$$

L_m = Liquid molar flux, lb mole/(ft²)(hr)

Thus, measurement of the mole fractions of odorant at the top and bottom of the column leads to the evaluation of K_{Ga} if the Henry's law constant is known. The criterion for a very slow reaction is that the fraction of absorbed gas which reacts before leaving the bottom of the column is small and the liquid remains saturated with unreacted gas.

3. Wet Scrubbing With a Slow Reaction

If the reaction between a scrubbing liquid and an absorbed odorant is appreciable for some fraction of dissolved odorant to react, but too slow for an appreciable amount of reaction to occur in the diffusion film, the problem can be simplified with the following assumptions:

- i. the reaction occurring in the diffusion film is negligible;
- ii. the reaction between the odorant and scrubbing reagent is irreversible;
- iii. the reagent concentration is very high relative to the odorant concentration and hence the reaction can be considered as a psuedo-first order process.

The reaction rate for an irreversible psuedo-first order chemical process is given by

$$r = k_1 A = k_1 \bar{p}_L x \quad (3-20)$$

where

r = Rate of reaction, lb mole/(ft³)(s)

k_1 = Rate constant of first order reaction, s^{-1}

A = Concentration of absorbed solute in liquid, lb mole/ft³

$\bar{\rho}_L$ = Average molar density of liquid, lb mole/ft³

x = Mole fraction of absorbed gas in liquid

The steady state rate of absorption would be

$$N_a = K_G a (y - H_e x) = k_1 \bar{\rho}_L x \quad (3-21)$$

Elimination of "x" gives

$$N_a = K_{GR} a y \quad (3-22)$$

where

$$\frac{1}{K_{GR} a} = \frac{1}{K_G a} + \frac{1}{k_1 \bar{\rho}_L} \quad (3-23)$$

With the "dilute gas" hypothesis, both the equilibrium and operating lines are straight. A substitution of Equation 3-22 into Equation 3-16 gives

$$K_{GR} a dz = -G_m dy / y \quad (3-24)$$

which can be integrated to yield

$$K_{GR} a = \frac{G_m}{Z} \ln(y_B / y_T) \quad (3-25)$$

Evaluation of mass transfer coefficients requires a further knowledge of the rate and mechanism of the chemical reaction. The criterion for testing that the reaction occurring

in the diffusion film is negligible is given by (23)

$$\frac{D_A k_1}{k_l^2} \ll \frac{k_1}{k_1 + k_2 a} \quad (3-26)$$

where

D_A = Diffusivity of dissolved solute in liquid, ft^2/hr

4. Wet Scrubbing With a Fast Reaction

In this case the reaction is fast and an appreciable fraction of dissolved odorant reacts in the diffusion film. It is common to assume that the reaction is irreversible and that the rate is high enough to insure that all of the absorbed gas reacts in the diffusion film and none diffuses in the unreacted state into the liquid. With $x = 0$, Equation 3-9 becomes

$$N = K_G y \quad (3-27)$$

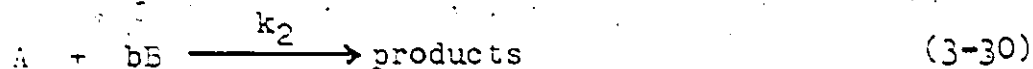
Substituting into Equation 3-16, again for dilute solutions, gives

$$K_G a dz = - G_m dy / y \quad (3-28)$$

Integrating over the column gives

$$K_G a = \frac{G_m}{Z} \ln(y_B / y_T) \quad (3-29)$$

The overall gas-side mass transfer coefficient, K_{ga} , can be calculated directly from the rate of absorption, without the necessity of accurately knowing the rate of reaction in the liquid phase. For a second order reaction



the condition to be satisfied if all of the dissolved gas reacts in the film and the concentration of unreacted absorbed gas in the bulk of the liquid is negligibly small is given by (23)

$$\frac{\sqrt{D_A k_2 B}}{k_L} < 10 \left(1 + \frac{D_B B}{b D_A A_i} \right) \quad (3-31)$$

where

D_B = Diffusivity of reagent in the liquid, ft^2/hr

b = Number of moles of reagent reacting with each mole of solute

5. The Effect of Chemical Reaction on the Rate of Absorption

Almost all the important processes involving odor removal by wet scrubbing depend on chemical reaction. It is therefore important to know by how much the chemical reaction increases the rate of absorption.

The factor by which the rate of odor absorption is

increased by virtue of chemical reaction is usually defined as the enhancement factor, ϕ , expressed as the ratio of the liquid-side mass transfer coefficient obtained with the chemical absorption to that obtained from physical absorption alone. The definition is expressed in terms of

$$\phi = \frac{(k_L)_{\text{chem.}}}{(k_L)_{\text{phys.}}} \quad (3-32)$$

or

$$\phi = \frac{(k_L a)_{\text{chem.}}}{(k_L a)_{\text{phys.}}} \quad (3-33)$$

where $()_{\text{chem.}}$ is the value from the absorption with chemical reaction, and $()_{\text{phys.}}$ is the value from scrubbing with water only.

IV. EXPERIMENTAL PROGRAM

A. Experimental Plan

1. Solubility Measurements

Solubilities of butyraldehyde and n-butyl mercaptan in water were determined at 1 atm for temperatures of 0°, 25° and 40° C with concentrations of the odorants in the gas phase varying from 0 to 500 ppm. In order to estimate hg values, solubilities of butyraldehyde and n-butyl mercaptan were also measured in 1 M salt solution.

2. Wet Scrubbing Measurements

Butyraldehyde and n-butyl mercaptan were scrubbed with up to 1.0 gpm of pure water at gas flow rates ranging from 10 to 25 cfm. The rates of removal of butyraldehyde and n-butyl mercaptan with aqueous sodium hypochlorite and potassium permanganate solutions were studied over the pH range 9 to 12 for oxidant concentrations varying from 0.01 to 0.20 % by weight.

B. Scrubbing System Equipment

A schematic diagram of the experimental equipment is shown in Figure 4-1. The odor scrubbing unit consists of four parts:

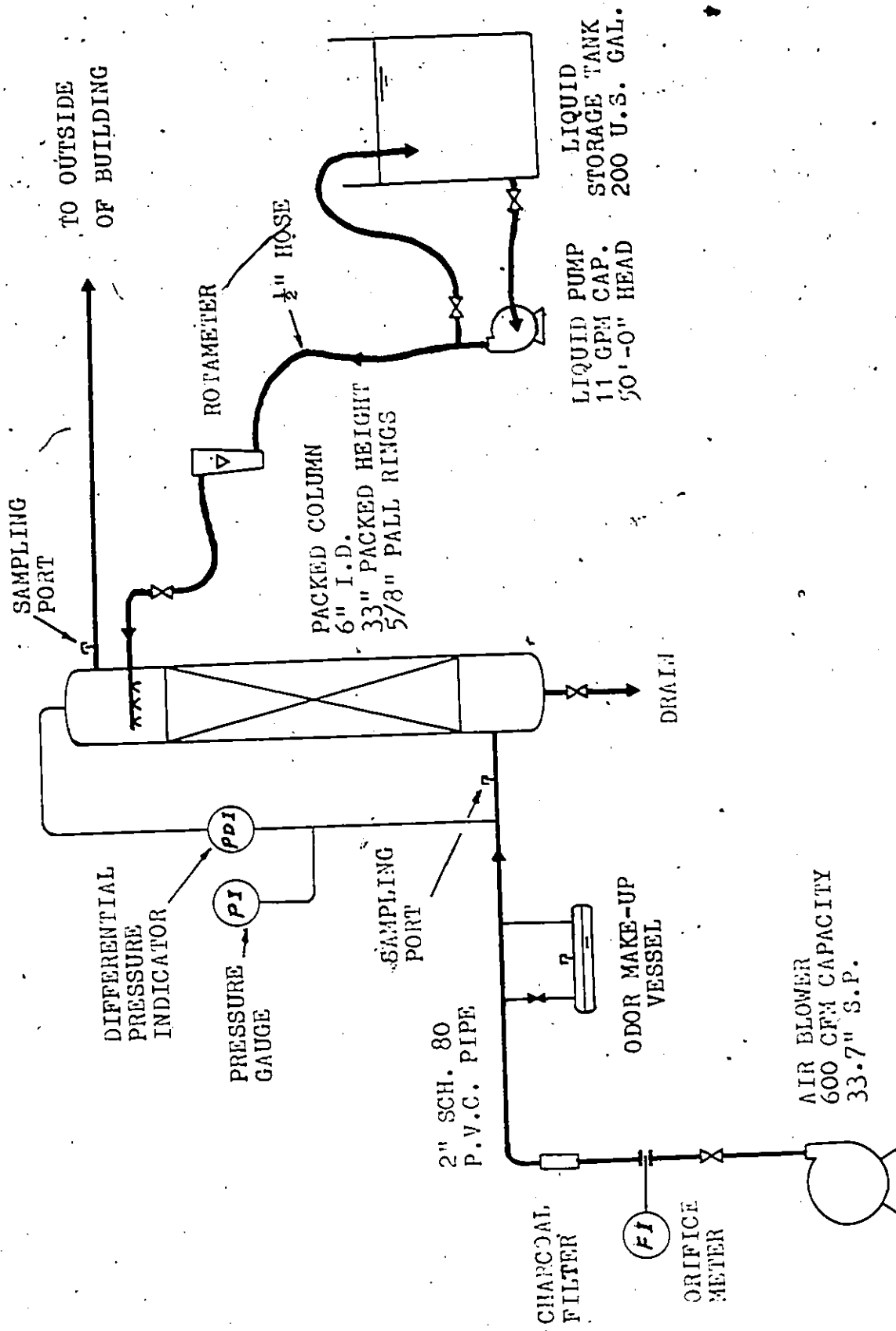


Figure 4-1. Schematic Diagram of Wet Scrubbing System

1. feed system,
2. packed tower,
3. effluent system,
4. sampling system.

1. Feed System

Air was supplied by an air blower with a 600 cfm capacity at 33.7"-water static pressure. The air flow rate was controlled by a gate valve and metered precisely by an orifice meter. Some of the air was bypassed to the odor make-up vessel containing the pure liquid odorant to be introduced to the main air line. Details of the odor make-up vessel are shown in Figure 4-2. The concentration of odorant in the air was set by adjusting the air flow rate to the odor make-up vessel. The main air line was constructed of 2" Schedule 80 PVC pipe.

The scrubbing liquid, stored in two 200 U.S. gallon plastic tanks, was circulated by means of a bronze pump with 11 gpm capacity at 50 feet of head. The liquid flow rate, controlled by adjusting the recirculation to the tank, was metered with a calibrated rotameter. The liquid line was a $\frac{1}{2}$ -inch flexible plastic hose.

2. Packed Tower

The column was constructed of 6" I. D. pyrex glass fittings as shown in Figure 4-3. The packing was supported

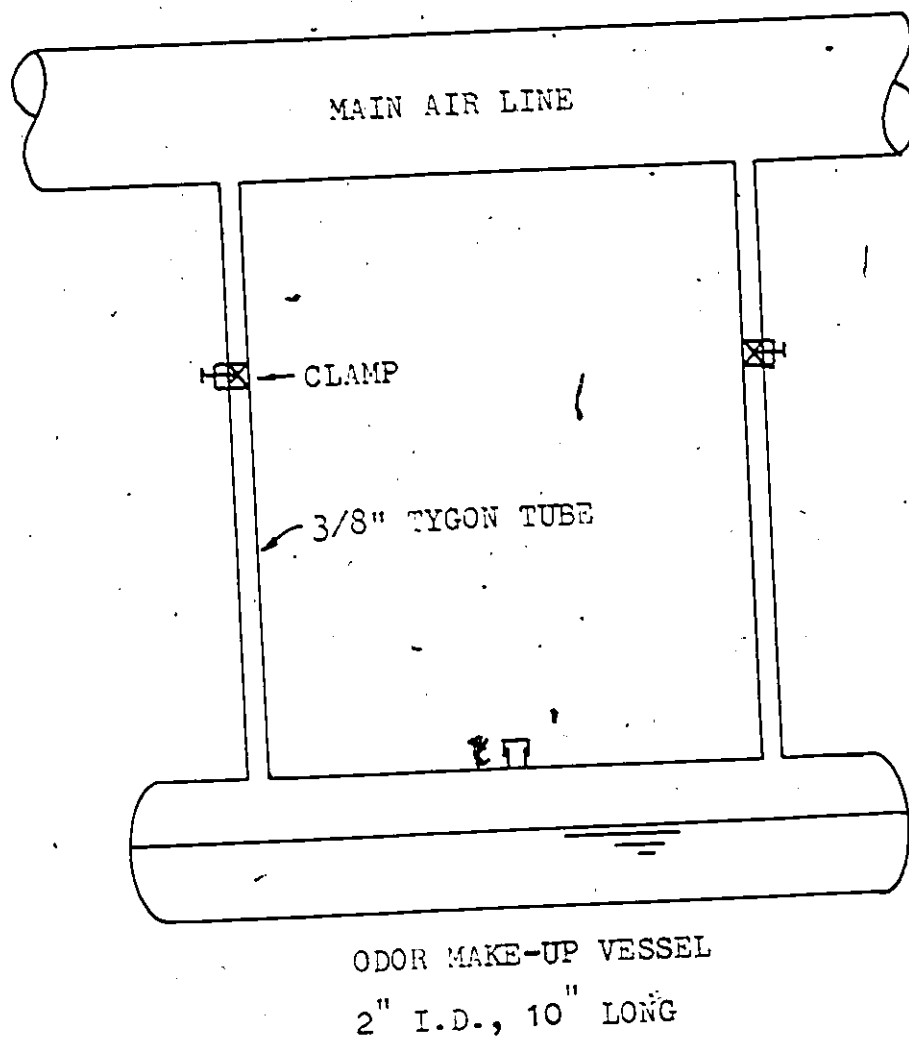
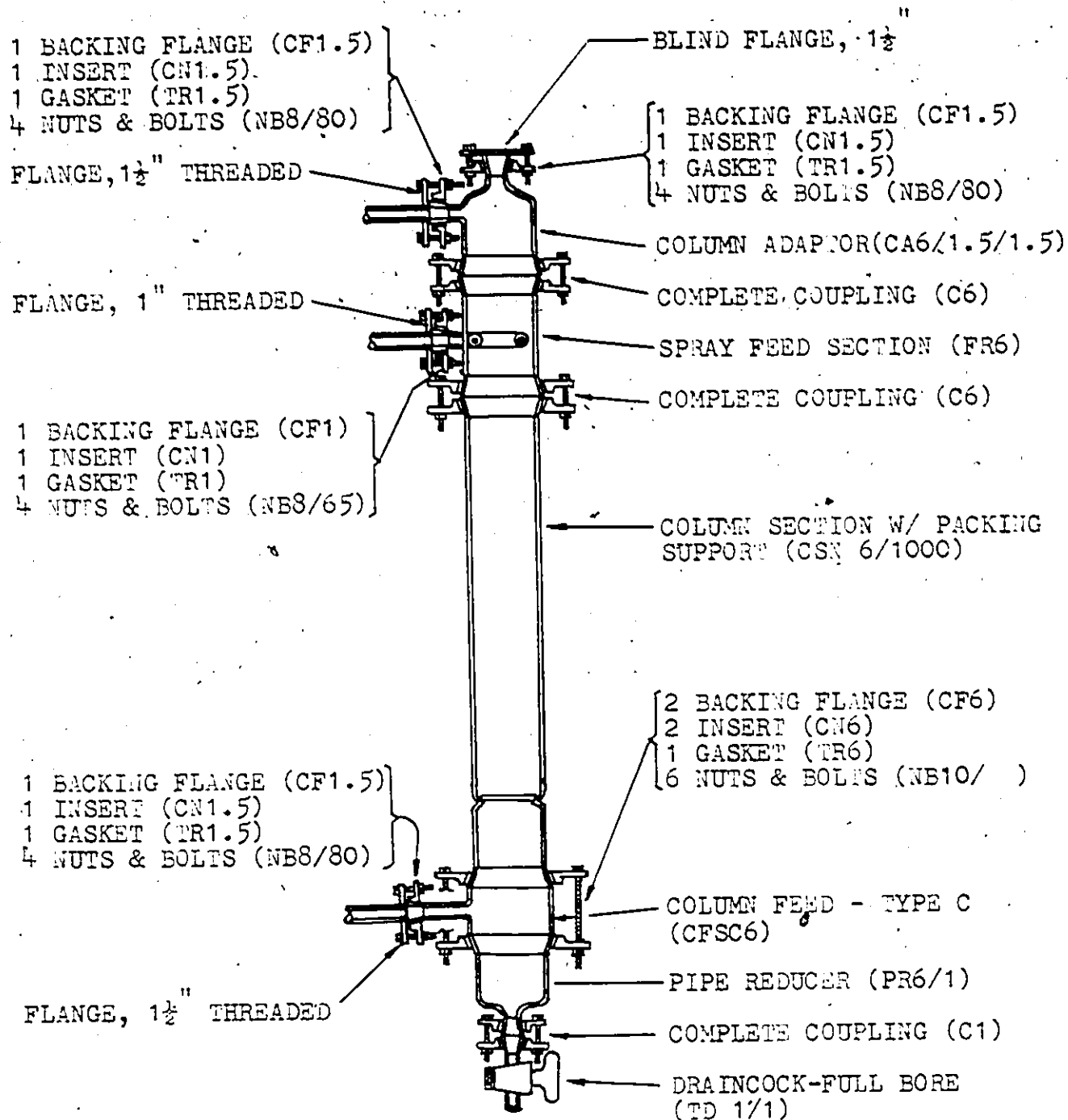


Figure 4-2. Odor Make-up Vessel



NOTE: () - Q. V. F. CATALOG NO.

Figure 4-3. Column Details

on a teflon plate whose cross-section was drilled with holes to provide 70 % void space. Many of the packings shown in Figure 4-4 have been used in industrial absorption systems. For the experimental tests 5/8" stainless steel Pall rings were packed to a height of 33 inches. The scrubbing liquid was distributed as a spray down the packing from a ring type sprayer at the top of the column. The odorous gas entered at the bottom of the column. A demister, installed at the top of the column, removed water drops which could interfere with the sampling system for the effluent gas. The pressure difference between the inlet and outlet of the column was measured with a manometer. Static pressure at the column inlet was monitored with a pressure gauge.

3. Effluent System

The outlet gas was vented to the outside of the building through a 2½" plastic pipe. The liquid effluent was collected in a surge tank and then drained through a 2" flexible plastic garden hose.

4. Sampling System

A schematic drawing of the sampling system is shown in Figure 4-5. Two 650-ml bottles were used to collect samples. Air samples were drawn from the inlet and outlet of the column

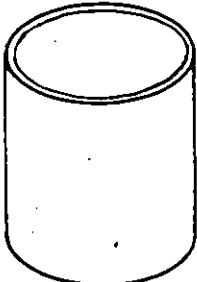
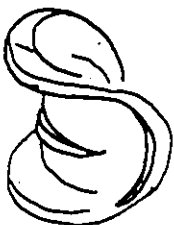

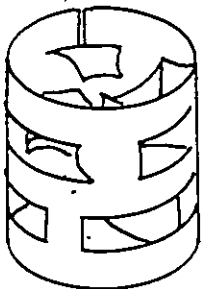
Packings	Application Features
<p>Raschig Rings</p> 	<p>Most popular type, usually cheaper per unit cost but sometimes less efficient than others. Available in widest variety of materials to fit services.</p>
<p>Berl Saddles</p> 	<p>More efficient than Raschig rings in most applications, but more costly.</p>
<p>Intelox Saddles</p> 	<p>One of most efficient packings, but more costly. Generally specified for aqueous systems when corrosion is a major factor.</p>
<p>Pall Rings</p> 	<p>Most efficient packing with lower pressure drop. Good liquid distribution, high capacity. Usually used in handling organic materials when there are no major corrosion problems. Available in metal, plastic, and ceramic.</p>

Figure 4-4. Some Typical Packings and Applications

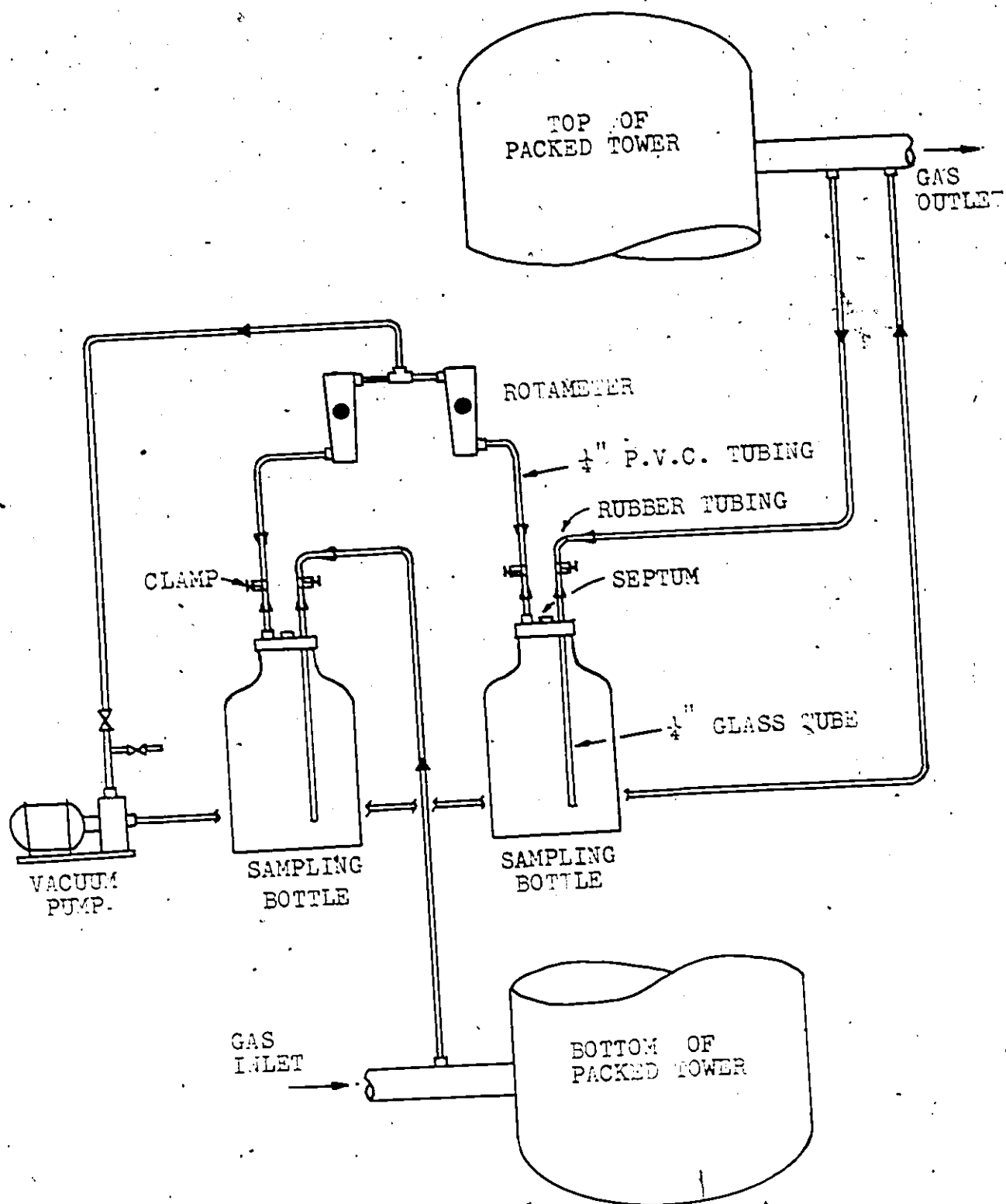


Figure 4-5. Gas Sampling System

through the sampling bottles with a vacuum pump. A separate rotameter was installed in each sampling line to indicate the flow rate and avoid back-mixing of the two samples.

C. Material Used

Scrubbing solutions were prepared from

- i. sodium hypochlorite, 16 % solution, technical grade, supplied by Lawrason Chemical Company;
- ii. potassium permanganate, powder, technical grade, supplied by Lawrason Chemical Company;
- iii. sodium hydroxide, pellet, laboratory grade, supplied by Fisher Scientific Company.

Odors were generated from

- i. butyraldehyde, 99 % , supplied by Aldrich Chemical Company;
- ii. n-butyl mercaptan, 98 %, supplied by Aldrich Chemical Company.

All analytical chemicals used in the experiments were A.C.S. grade and supplied by Fisher Scientific Company.

D. Analytical Methods

1. Determination of Odorant Concentrations

The concentrations of butyraldehyde and n-butyl mercaptan were determined with a Varian Aerograph series 1520 gas chromatograph equipped with a hydrogen flame ionization detector.

A 10-foot long column of 1/8" O. D. stainless steel tubing packed with 10 % carbowax 20-M on 100-200 mesh chromosorb G, as proposed by Murthy⁽¹⁷⁾, was used for analytical purposes. The oven temperature for butyraldehyde was 100° C and 125° C for n-butyl mercaptan. The nitrogen carrier gas was maintained at a flow rate of 25 ml/min with an inlet pressure of 80 psig. The hydrogen flow rate was regulated at 25 ml/min while the oxygen flow to the detector was 250 ml/min.

2. Determination of NaOCl Concentrations (25)

The concentration of NaOCl in the scrubbing liquid was determined by volumetric titration with standard iodine solution. For a 50-ml sample, 10 ml of 1 % NaOH solution was added to prevent any local acidity which could interfere with the titration. The sodium hypochlorite was oxidized by adding an excess amount (usually 25 ml) of standard 0.1 N arsenious oxide solution. A sufficient excess of sodium bicarbonate was added to keep the solution saturated throughout the subsequent titration. The excess arsenious oxide was titrated with standard 0.1 N iodine solution, using starch as an indicator.

3. Determination of KMnO₄ Concentrations (26)

The concentration of KMnO₄ was determined with standard arsenious oxide solution. To a known volume (usually 25 ml)

of standard 0.01 N arsenious oxide solution, 5 ml of pure concentrated hydrochloric acid was added to make the solution acidic. Before titration, 1 drop of 0.0025 M potassium iodide was added to accelerate the rate of reaction of arsenic acid with permanganate. This system was titrated with potassium permanganate solution to a permanent faint pink colour.

4. Determination of Alkaline Concentrations

Alkaline concentrations were determined as pH values with a Fisher Accumet 120 pH meter. The pH meter was calibrated previously with standard pH 7 and pH 10 solutions.

E. Experimental Procedure

1. Solubility Measurements

Bottles of the type shown in Figure 4-6 were filled with different volumes of water and then closed with caps. A few micro-liters of the pure liquid odorants were injected into each bottle with a 10 micro-liter gas tight syringe. These bottles were put into a water bath for the measurements of solubility at 25° and 40° C or an ice bath for that at 0° C. In order to insure that equilibrium was established, these bottles were kept at the appropriate temperatures over night. The concentrations of odorants in both the gas and liquid phases were determined by gas chromatography. Calibration standards

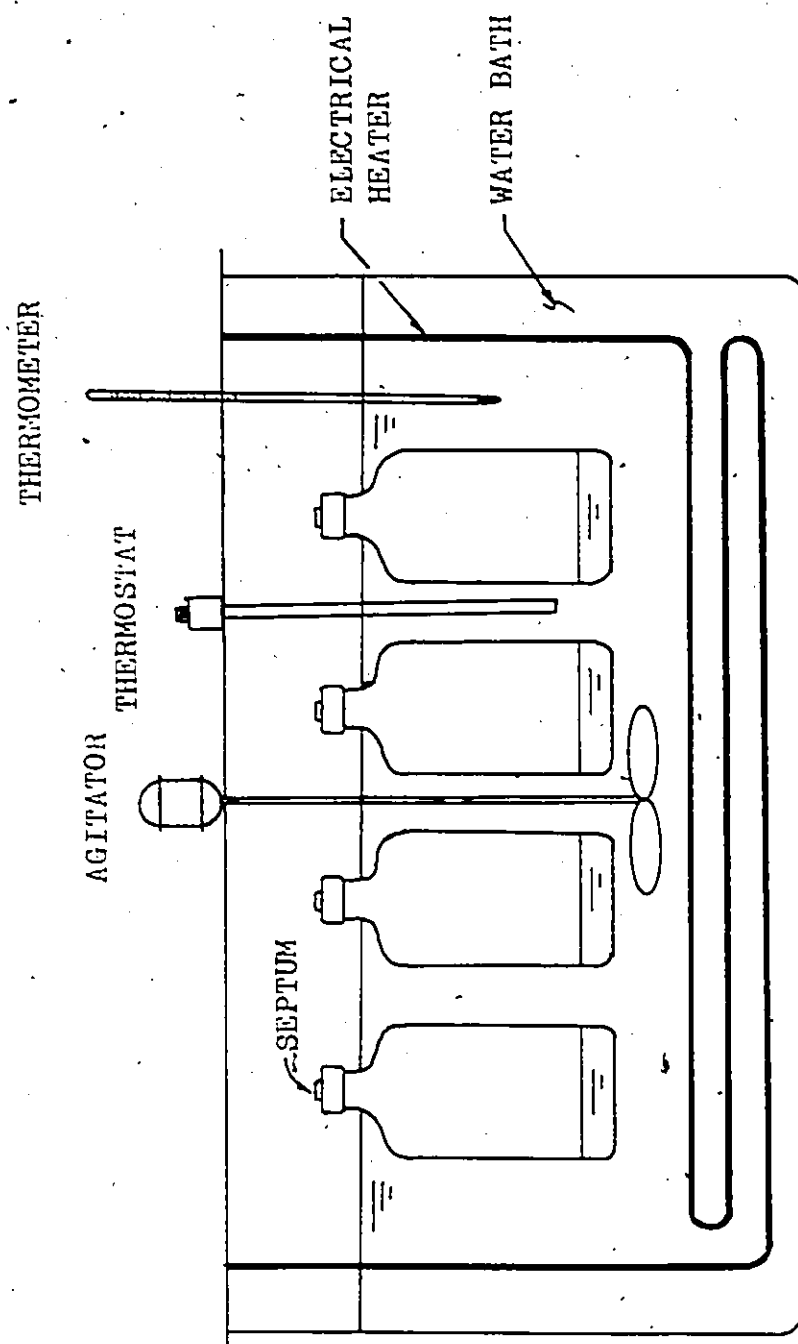


Figure 4-6. Solubility Measurement Apparatus

for the gas chromatograph were made by injecting known amounts of pure liquid odorant into bottles containing specific volumes of air or water.

2. Wet Scrubbing Tests

Scrubbing solutions were prepared in advance. The reagent concentrations were determined by volumetric titration and the alkalinity levels were evaluated with a pH meter. To start the scrubbing system, the liquid pump was turned on and the liquid flow was adjusted to the desired rate. After the air blower was started, the gas flow rate was set to the desired value. Odorant concentrations were found by gas chromatography and then adjusted to the desired level by controlling the bypass flow. A check was made of various gas and liquid flow rates during a run. The air pressure at the column inlet and the pressure difference across the column were recorded. About 45 minutes were required for steady state conditions to be established. For taking samples, the vacuum pump was turned on and both inlet lines to the sampling bottles were closed with clamps. The bottles were evacuated for 5 minutes. Sample collection was started by opening the sampling inlet valves. The samples were drawn through the sampling bottles and sent back to the gas outlet line as shown in Figure 4-4. After a 10 minute sampling time, the scrubbing system was shutdown.

by stopping the pump and blower. A 2-ml sample was taken from the bottles with a 5-ml gas tight syringe for analysis by gas chromatography.

V. RESULTS AND DISCUSSION

The results of solubility and scrubbing runs are presented in this chapter. A complete error analysis for the system is given in Appendix I. The solubility data are estimated to be accurate to $\pm 2.5\%$ and scrubbing results to $\pm 5.1\%$.

A. Solubility Measurements

The method of measuring solubilities, as described in Chapter IV, was checked by using it to evaluate the vapor pressure of butyraldehyde. The consistent results, shown in Figure II-1 of Appendix II, indicate that this technique is feasible and reliable. The experimentally determined solubilities of butyraldehyde and n-butyl mercaptan are tabulated in Appendix III. An overall material balance on the system, based on gas and liquid analysis, showed satisfactory agreement with experimental results. The solubilities of butyraldehyde and n-butyl mercaptan in pure water at 0° , 25° and 40° C are shown in Figures 5-1 and 5-2. Both compounds obeyed Henry's law over the temperature and pressure ranges involved. Butyraldehyde is slightly soluble in water, but n-butyl mercaptan is almost completely insoluble.

For the determination of the solubility in 1 M salt solution, it was not possible to establish the odorant concentration in the salt solutions by gas chromatography. Consequently, the concentrations of butyraldehyde and n-butyl mercaptan in salt solutions were evaluated from the difference between the total amount of odorant injected and the amount of odorant in the gas

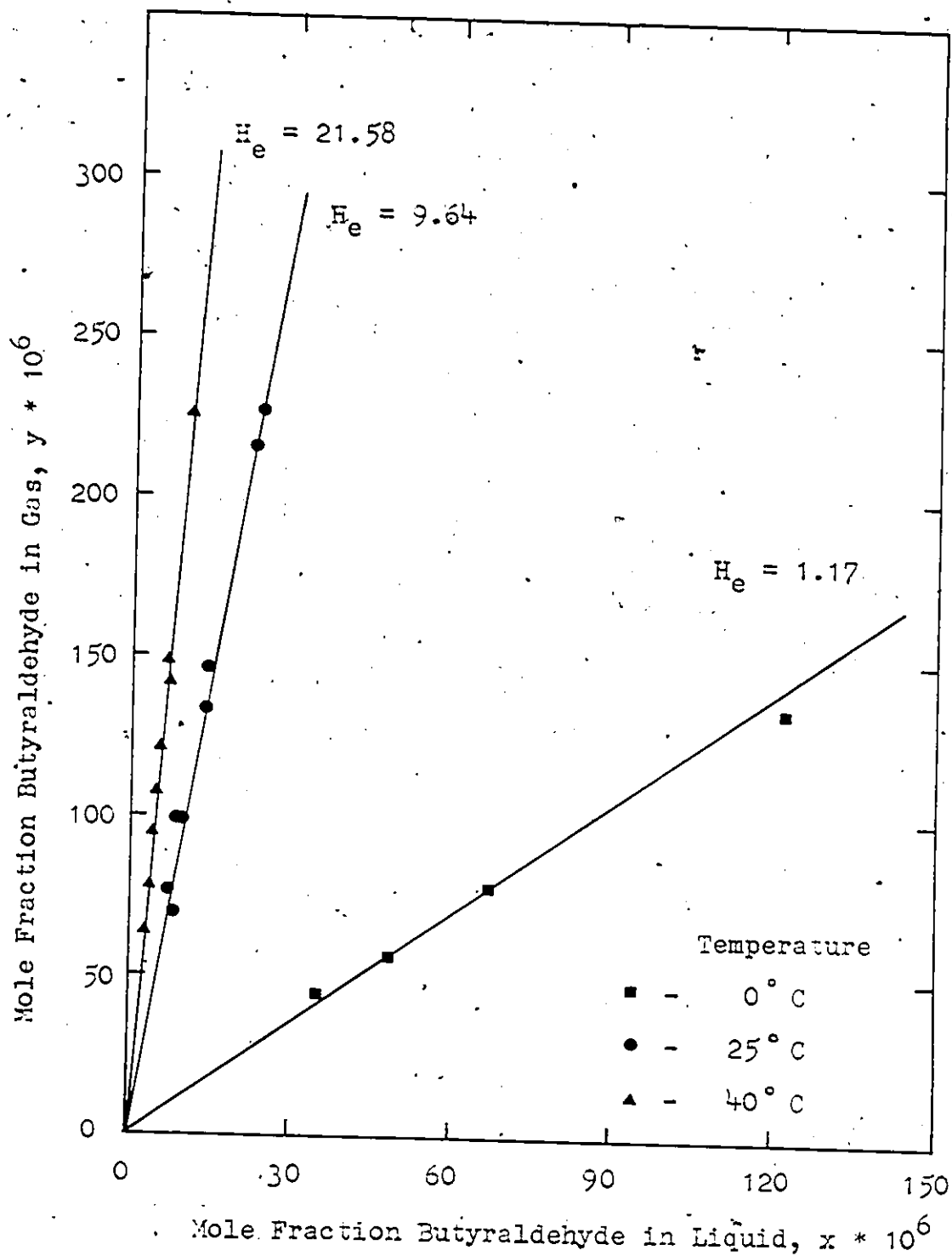


Figure 5-1. Solubility of Butyraldehyde in Water at 1 atm

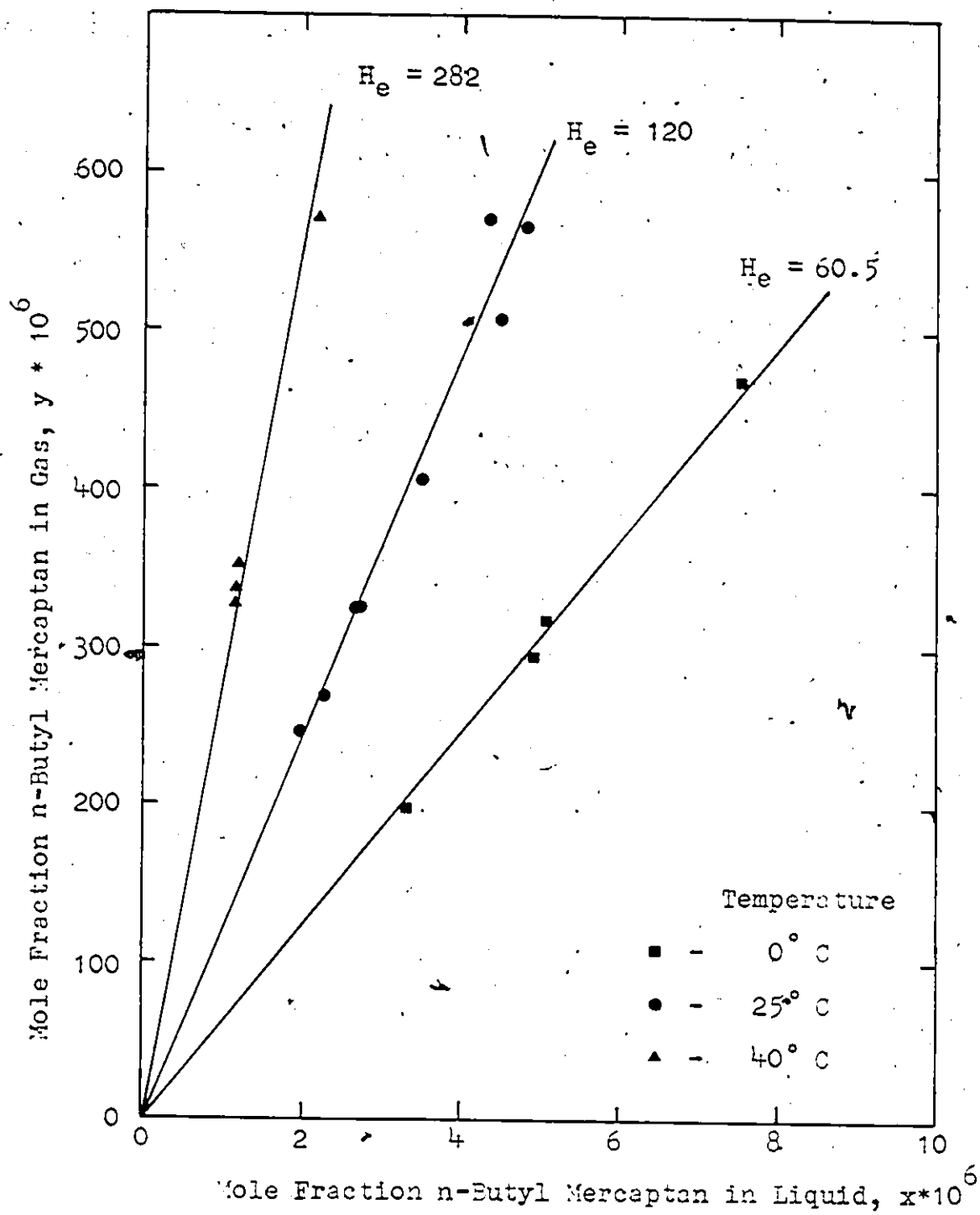


Figure 5-2. Solubility of n-Butyl Mercaptan in Water at 1 atm

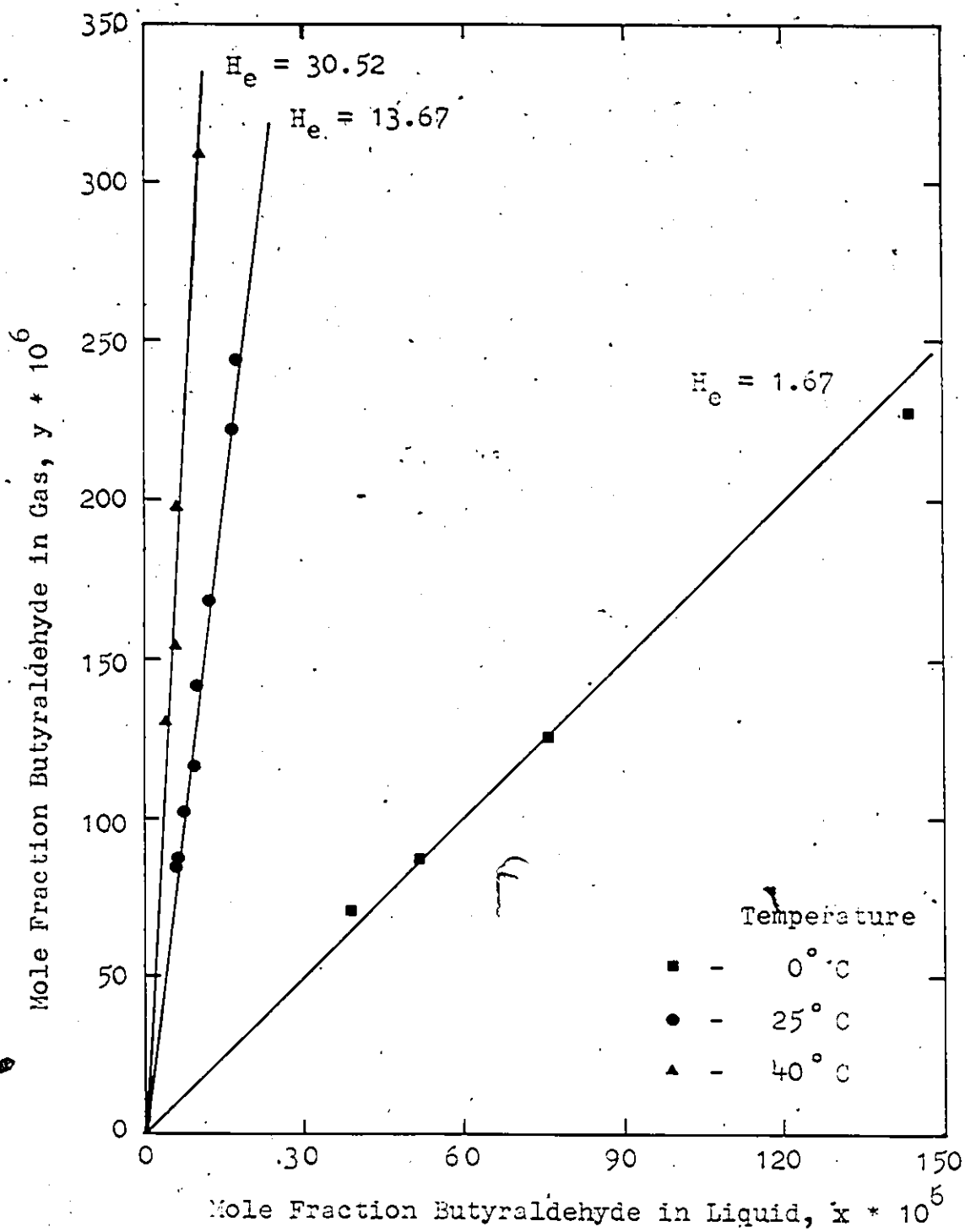


Figure 5-3. Solubility of Butyraldehyde in 1 M NaCl Solution at 1 atm

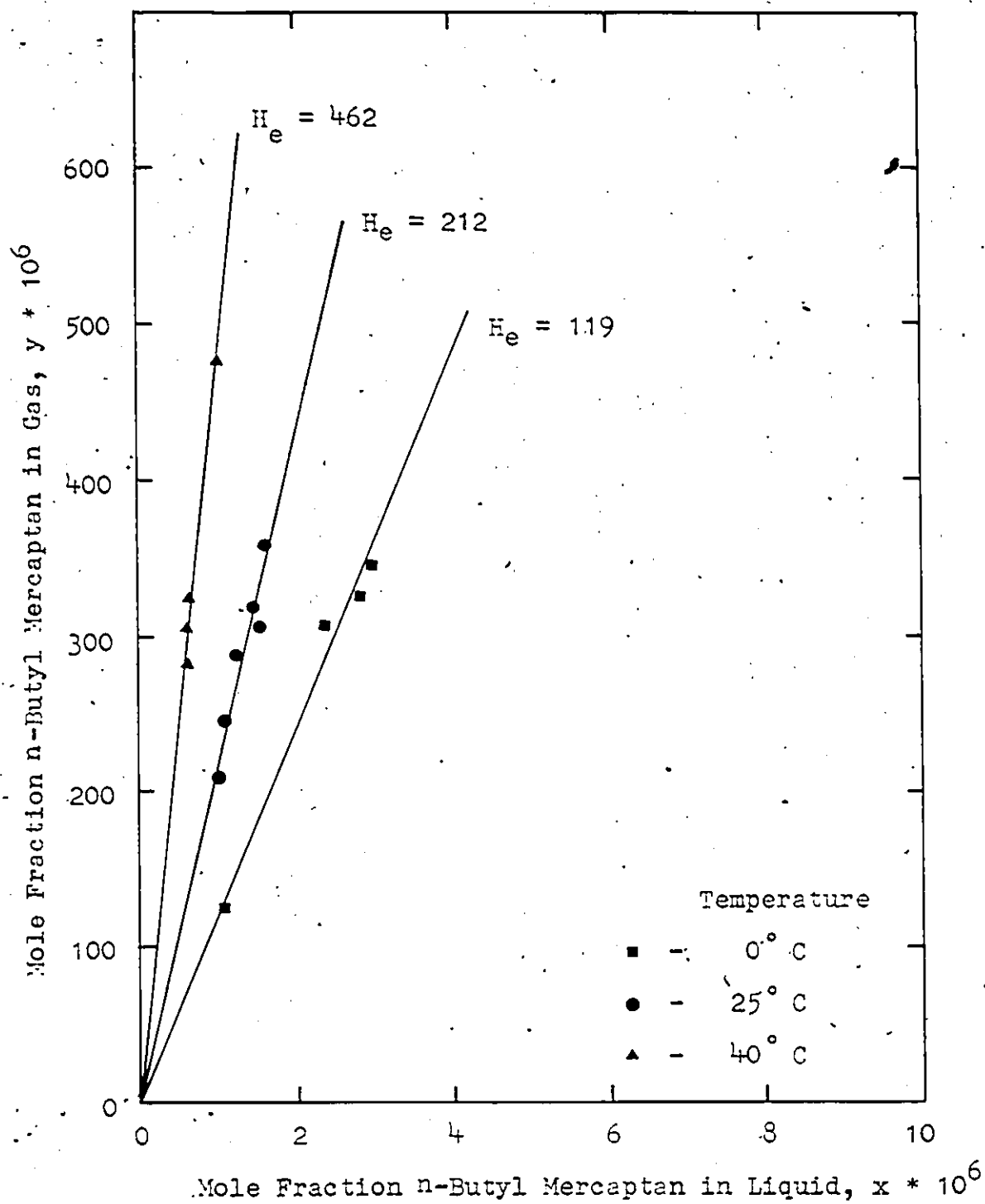


Figure 5-4. Solubility of n-Butyl Mercaptan in 1 M NaCl Solution at 1 atm

phase. The solubilities of butyraldehyde and n-butyl mercaptan in 1 M NaCl solution are plotted in Figures 5-3 and 5-4.

The solubilities of the odorant in alkaline sodium hypochlorite and potassium permanganate solutions were estimated from Equation 3-6. The values of h_a and h_c were taken from Table 3-1. For h_a of ClO^- , which is not available in the literature, the h_a of ClO_2^- was used. The values of h_g for butyraldehyde and n-butyl mercaptan were estimated from solubilities in 1 M NaCl solution and are listed in Table 5-1. The Henry's law constants calculated from Equation 3-6 for butyraldehyde and n-butyl mercaptan in the various concentrations of alkaline sodium hypochlorite and alkaline potassium permanganate solutions used in this study differ only by about 1 % from the Henry's law constants in water. This indicates that the electrolyte concentrations of the scrubbing solutions are too low to affect the solubilities of the odorant in water.

B. Wet Scrubbing Measurements

Odor removal by scrubbing with water and chemical reagent solutions was carried out in the packed bed scrubber. The liquid temperature was adjusted in the tank with cold water to about 23° C. The average gas temperature was about 27° C. A slight maldistribution of liquid over the packing was observed. It appeared that the sprayer ring at the top of the tower was not welded evenly. As a result, the sprayed liquid channelled down one side and a small portion of the packing at the top of the packed bed was found to be dry and inactive.

Compound	Temperature, °C	h_g
Butyraldehyde	0	- 0.1633
	25	- 0.1716
	40	- 0.1723
n-Butyl Mercaptan	0	- 0.0296
	25	- 0.0761
	40	- 0.1089

Table 5-1. Values of h_g for Butyraldehyde and n-Butyl Mercaptan

1. Wet Scrubbing With Water

The results of scrubbing butyraldehyde and n-butyl mercaptan with pure water are shown in Tables 5-2 and 5-3. Because butyraldehyde is much more soluble in water than n-butyl mercaptan, a higher removal efficiency of butyraldehyde was observed. The overall gas-side mass transfer coefficients, calculated from Equation 3-13, were plotted against different gas flow rates as shown in Figures 5-5 and 5-6. It has been observed^(27,28,29) that the gas-side mass transfer coefficient is dependent on gas and liquid flow rates; whereas the liquid side mass transfer coefficient will vary with changes in the liquid flow rate only. For both butyraldehyde and n-butyl mercaptan, overall gas-side mass transfer coefficients were found not to increase appreciably with increasing gas flow rate. This behavior indicates that the liquid-side mass transfer resistance is controlling the rate of absorption and the gas-side mass transfer resistance is negligible.

Several semiempirical correlations for liquid-side mass transfer coefficient are available in the literatures^(27,28,30). The general correlation given by Norman⁽²⁸⁾ for different size packing (3/8" to 2" Raschig rings and 1/2" to 1 1/2" Berl Saddles) is

$$k_L a = 120 D_A \left(\frac{L}{\mu_L} \right)^{0.75} \left(\frac{\mu_L}{\rho_L D_A} \right)^{0.5} \quad (5-1)$$

Water	Gas			Removal Efficiency %
	Flow Rate gpm	Flow Rate cfm	Inlet Conc. $\frac{\text{lb}}{\text{ft}^3} \times 10^6$	Outlet Conc. $\frac{\text{lb}}{\text{ft}^3} \times 10^6$
0.5		10.0	206.3	95.8
0.5		15.0	270.3	164.6
0.5		20.0	233.3	158.3
0.5		25.0	310.4	229.2
1.0		10.0	183.8	50.0
1.0		15.0	312.5	129.2
1.0		20.0	206.3	110.4
1.0		20.0	250.0	133.3
1.0		25.0	262.5	162.5
				53.6
				39.2
				32.1
				26.2
				72.7
				58.7
				46.5
				46.7
				38.1

Table 5-2. Results of Scrubbing Butyraldehyde With Water

Water	Gas			Removal Efficiency %
	Flow Rate gpm	Flow Rate cfm	Inlet Conc. $y \times 10^6$	Outlet Conc. $y \times 10^6$
0.5	10.0	183.5	173.2	5.6
0.5	15.0	210.0	202.1	3.9
0.5	20.0	169.1	164.3	2.8
0.5	25.0	161.3	157.6	2.3
1.0	10.0	178.9	161.6	9.5
1.0	15.0	183.8	171.8	6.5
1.0	20.0	168.4	160.1	4.9
1.0	25.0	171.0	164.3	3.9

Table 5-3. Results of Scrubbing n-Butyl Mercaptan With Water

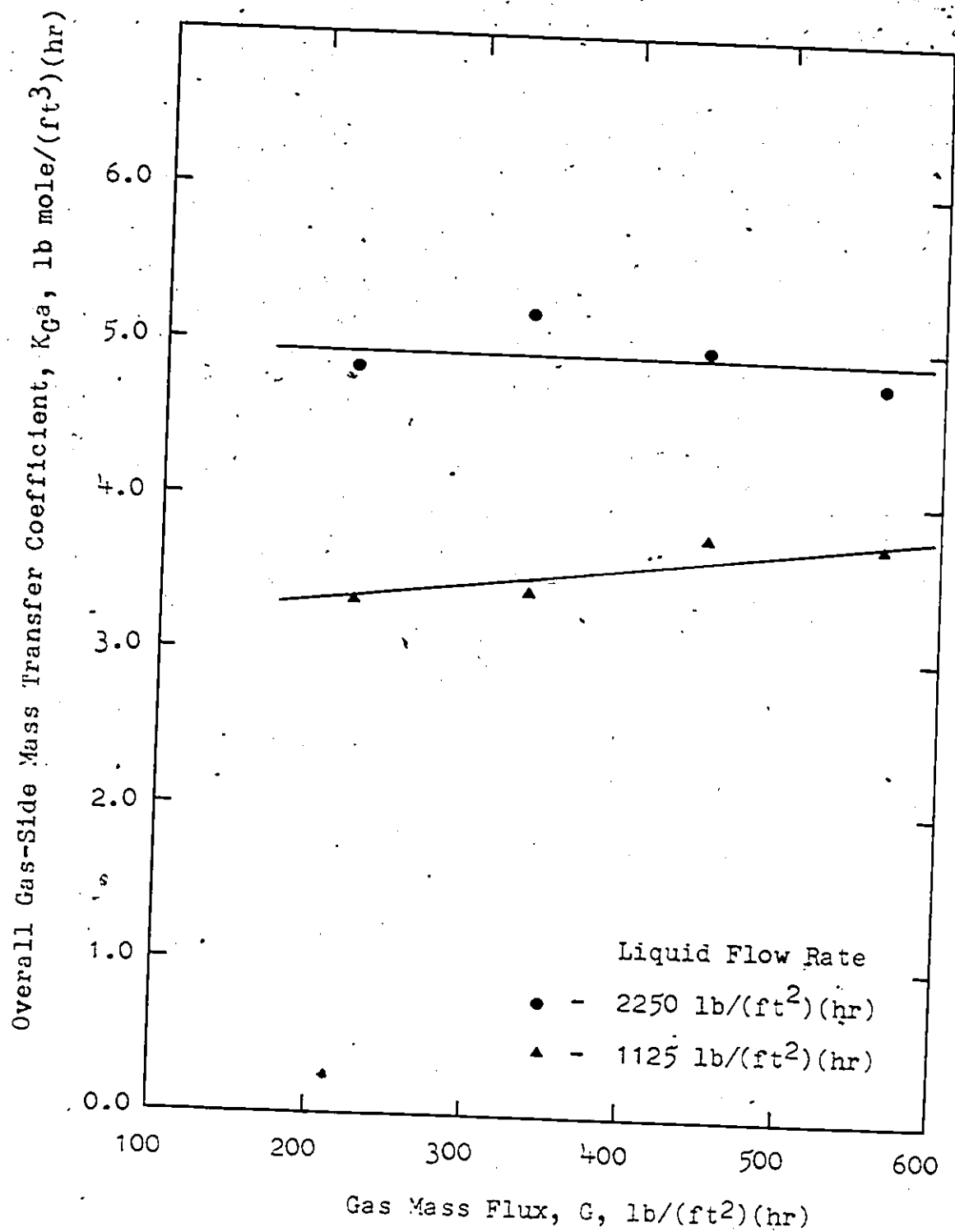


Figure 5-5. Effect of Gas Flow Rate on Overall Gas-Side Mass Transfer Coefficient for Scrubbing Butyraldehyde With Water at 1 atm and 25° C

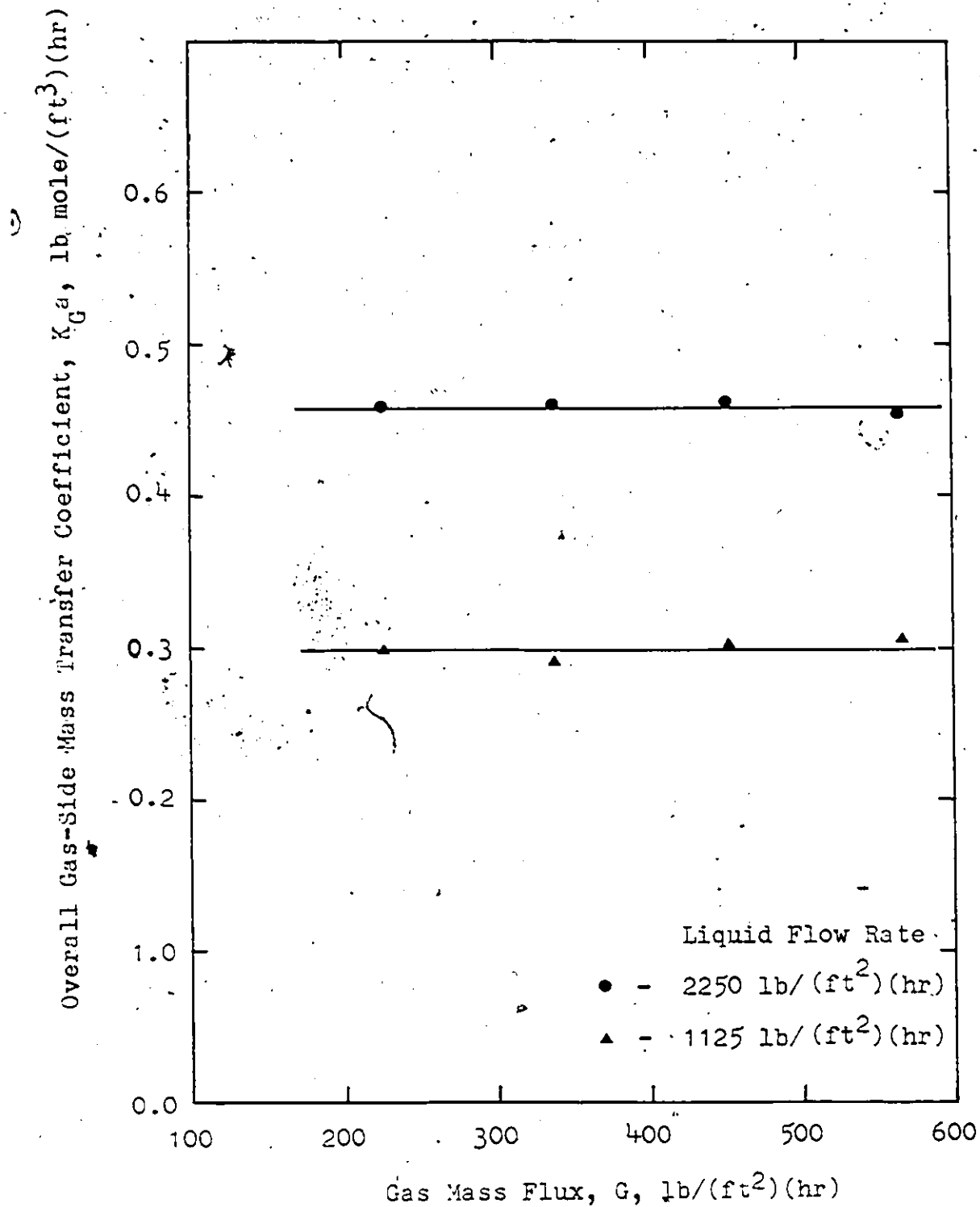


Figure 5-6. Effect of Gas Flow Rate on Overall Gas-Side Mass Transfer Coefficient for Scrubbing n-Butyl Mercaptan With Water at 1 atm and 25° C

where

D_A = Diffusivity of the dissolved solute in liquid, ft^2/hr

L = Liquid mass flux, $\text{lb}/(\text{ft}^2)(\text{hr})$

μ_L = Viscosity of liquid, $\text{lb}/(\text{ft})(\text{hr})$

ρ_L = Density of liquid, lb/ft^3

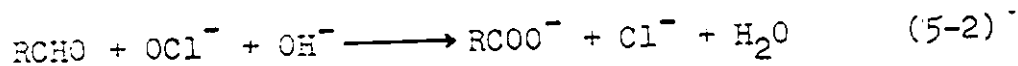
The values obtained experimentally and from Norman's correlation are listed in Table 5-4. The estimated values of the liquid-side mass transfer coefficient are roughly half of the experimental magnitudes. Perhaps Pall rings can achieve much higher efficiencies than Raschig rings or Berl saddles. However, for a 15 cfm gas flow rate and 0.5 gpm water flow rate a 39.2 % removal of butyraldehyde is compatible with the ³⁰(1) to 50 % removal of valeraldehyde obtained by Doty et. al.

2. Wet Scrubbing With Alkaline Sodium Hypochlorite

Solutions

a. Removal of Butyraldehyde

The oxidation of aldehydes by alkaline sodium hypochlorite solutions is similar to that achieved by aqueous bromine solutions. The general process can be described in terms of



The results of scrubbing butyraldehyde with alkaline sodium hypochlorite solutions are shown in Table 5-5. It seems

Compound	Liquid Flow Rate		k_{La} Experimental Value lb mole/(ft ³)(hr)	k_{La} Norman's Correlation lb mole/(ft ³)(hr)	Difference %
	gpm	lb/(ft ²)(hr)			
Butyraldehyde	1.0	2500	47.5	27.3	42.2
	0.5	1250	34.3	16.2	52.8
n-Butyl Mercaptan	1.0	2500	54.9	25.2	53.7
	0.5	1250	36.0	15.1	58.1

Table 5-4. Comparisons of Experimental k_{La} Values with Norman's Correlation

Liquid					Gas			Removal Efficiency %
Flow Rate gpm	Inlet		Outlet		Flow Rate cfm	Inlet Conc. $y \times 10^6$	Outlet Conc. $y \times 10^6$	
	NaOCl g/100ml	pH	NaOCl g/100ml	pH				
1.0	0.0107	9.0	0.0103	8.9	20.0	196.4	98.2	50.0
1.0	0.0107	9.9	0.0103	9.8	20.0	218.2	105.5	51.6
1.0	0.0107	11.0	0.0107	10.9	20.0	167.3	80.0	52.1
1.0	0.0107	12.0	0.0097	12.0	20.0	243.6	98.2	59.6
1.0	0.0107	11.0	0.0107	10.9	20.0	167.3	80.0	52.1
1.0	0.030	11.0	0.030	10.9	20.0	181.8	87.3	52.0
1.0	0.060	11.0	0.058	10.9	20.0	167.3	76.4	54.3
1.0	0.117	11.1	0.110	11.0	20.0	236.4	101.8	56.9

Table 5-5. Results of Scrubbing Butyraldehyde With Alkaline NaOCl Solutions

that the removal effectiveness of the hypochlorite is not much higher than that of pure water. Since the consumption of hypochlorite along the column is negligibly small, the rate of oxidation of butyraldehyde can be considered to be very slow. The effects of hypochlorite and alkaline concentrations on the enhancement factor are plotted in Figures 5-7 and 5-8. The enhancement factor increases slightly with increasing hypochlorite concentrations. An increase in the hypochlorite concentration should increase the rate of the reaction and hence increase the rate of absorption. A negative effect on the absorption rate at high NaOCl concentration was found by Murthy⁽¹⁷⁾. This can be explained by the diffusivity of the absorbed gas in solution being decreased at high NaOCl concentrations. As a result, an increase in hypochlorite concentration may not always enhance the rate of absorption. At low pH values (from 9 to 11) the influence of the alkaline concentration on the enhancement factor is very slight, but it increases gradually with increasing pH. At pH value above 11, an increase in the enhancement factor with increasing alkaline concentration is obvious owing to the increase in the formation of aldehyde hydrate which is oxidized much more rapidly than the neutral aldehyde.

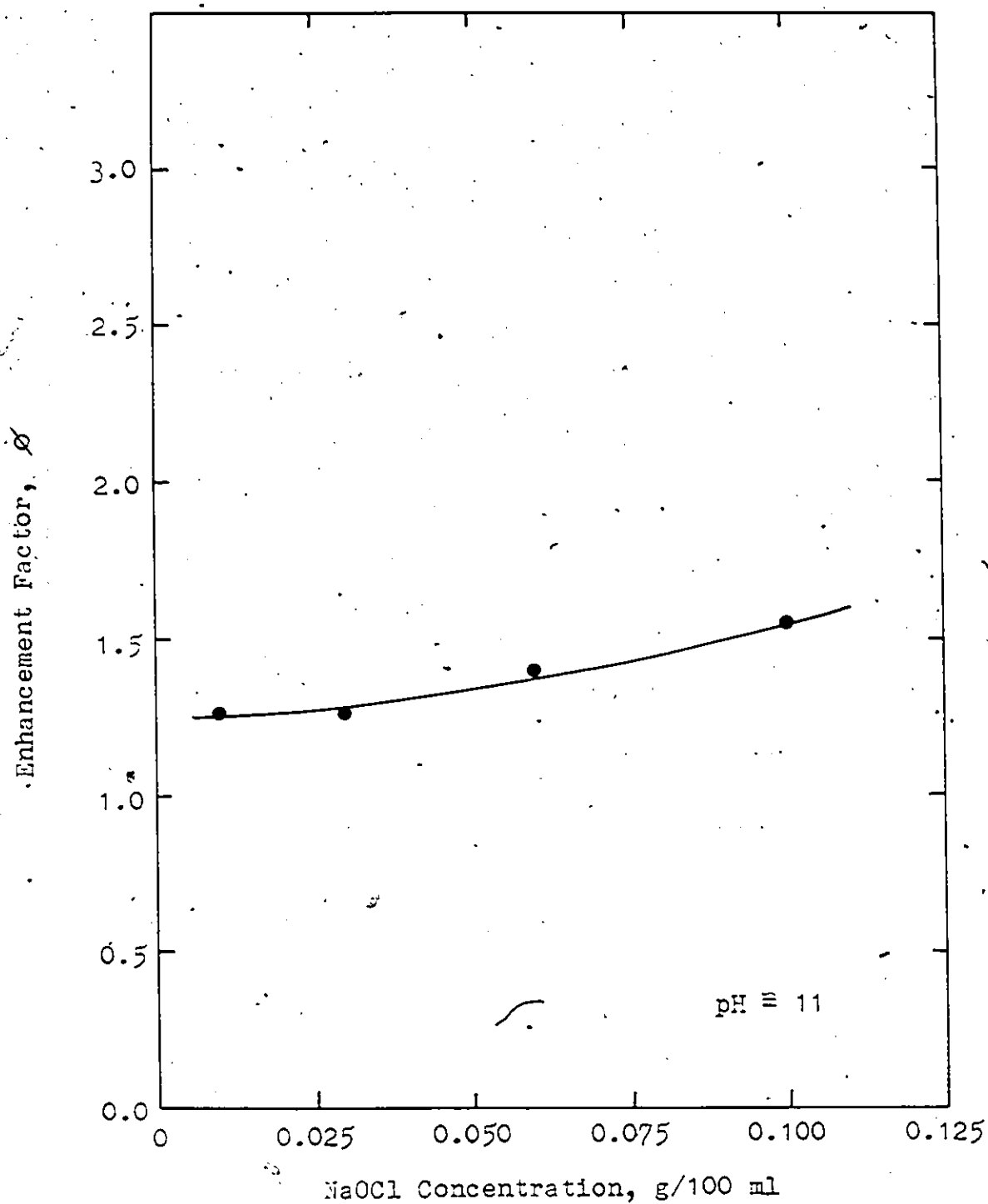


Figure 5-7. Effect of NaOCl Concentration on Enhancement Factor for Scrubbing Butyraldehyde With Alkaline Sodium Hypochlorite Solutions at 1 atm and 25 °C

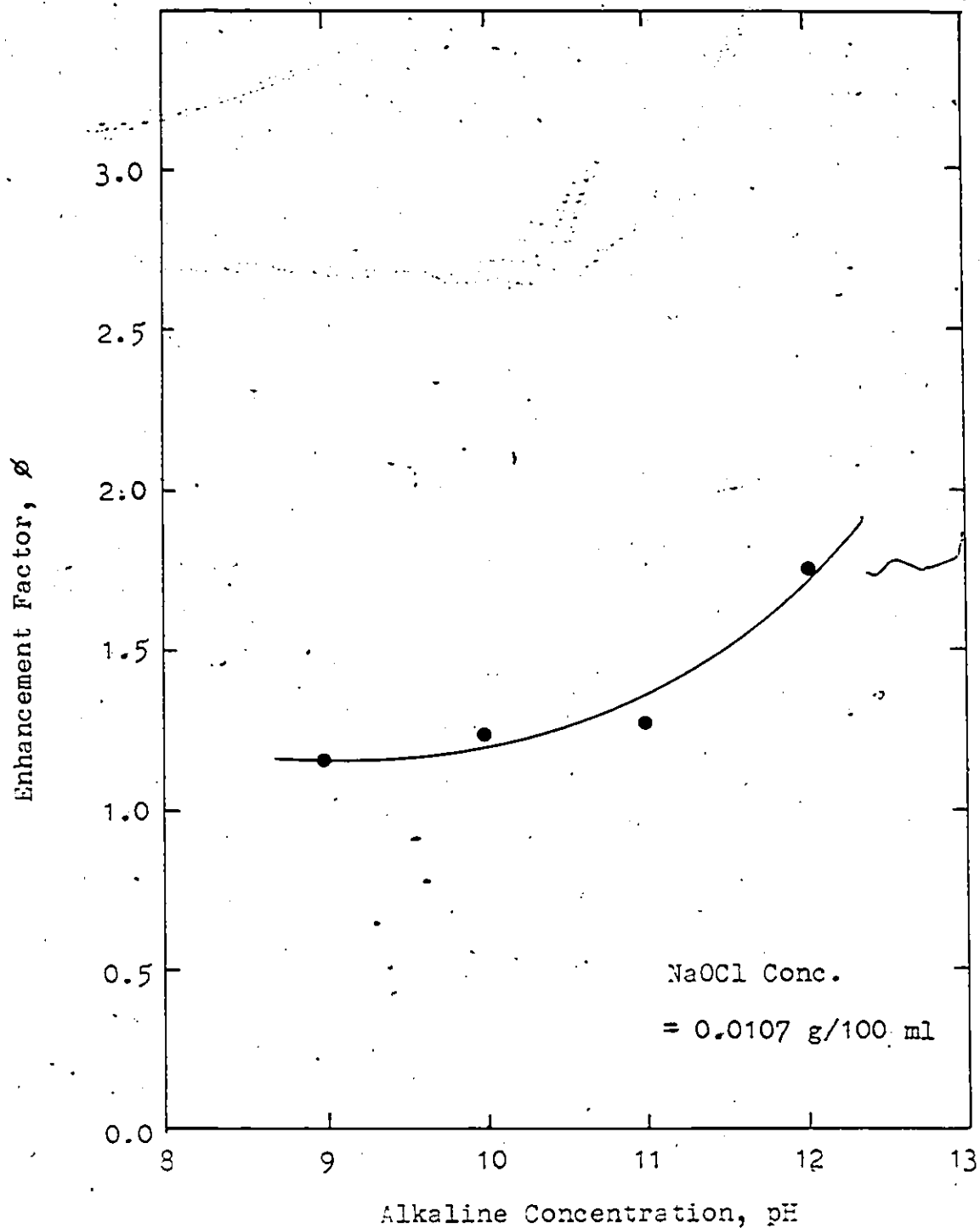
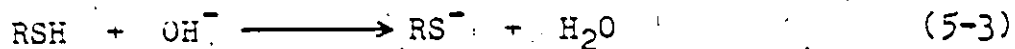


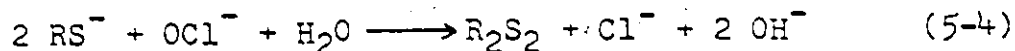
Figure 5-8. Effect of Alkaline Concentration on Enhancement Factor for Scrubbing Butyraldehyde With Alkaline Sodium Hypochlorite Solutions at 1 atm and 25° C

b. Removal of n-Butyl Mercaptan

In basic solution, mercaptans dissolve into the liquid phase with the formation of mercaptides according to



The mercaptides are oxidized to disulfides by hypochlorite as illustrated by the general process



Some sulfonates may result from direct oxidation of mercaptans or by further oxidation of disulfides.

The results of scrubbing n-butyl mercaptan with alkaline sodium hypochlorite solutions are listed in Table 5-6. A high removal efficiency of n-butyl mercaptan indicates that the reaction occurring in the scrubbing system is fast. The effects of hypochlorite and alkaline concentrations on the enhancement factor are shown in Figures 5-9 and 5-10. The enhancement factor increased rapidly when the hypochlorite concentrations were varied from 0.01 to 0.06 %, but increased only slightly when NaOCl concentrations exceeded 0.06%. A positive effect of hypochlorite concentration on the rate of absorption for removal of mercaptans was also found by Murthy⁽¹⁷⁾. With increasing alkaline concentrations, the enhancement factor is increased slowly at low pH values (from 9 to 11). A significant improvement in odorant removal occurs when the pH exceeds 11 due to the

Liquid					Gas			Removal Efficiency %
Flow Rate gpm	Inlet		Outlet		Flow Rate cfm	Inlet Conc. y * 10 ⁶	Outlet Conc. y * 10 ⁶	
	NaOCl g/100ml	pH	NaOCl g/100ml	pH				
0.5	0.0109	9.1	0.0018	8.3	20.0	162.0	72.0	55.6
0.5	0.0109	10.1	0.0013	9.8	20.0	159.0	63.0	60.4
0.5	0.0109	10.6	0.0013	10.4	20.0	150.0	48.0	68.0
0.5	0.0107	11.0	0.0012	10.8	20.0	167.6	42.6	74.6
0.5	0.0109	12.0	0.0000	11.9	20.0	174.0	15.0	91.4
0.5	0.0109	10.6	0.0013	10.4	20.0	150.0	48.0	68.0
0.5	0.0317	10.6	0.0224	10.3	20.0	170.6	19.5	88.6
0.5	0.0610	10.7	0.036	10.0	20.0	205.9	12.0	94.1
0.5	0.104	10.6	0.075	9.7	20.0	223.5	11.5	94.9

Table 5-6. Results of Scrubbing n-Butyl Mercaptan With Alkaline NaOCl Solutions

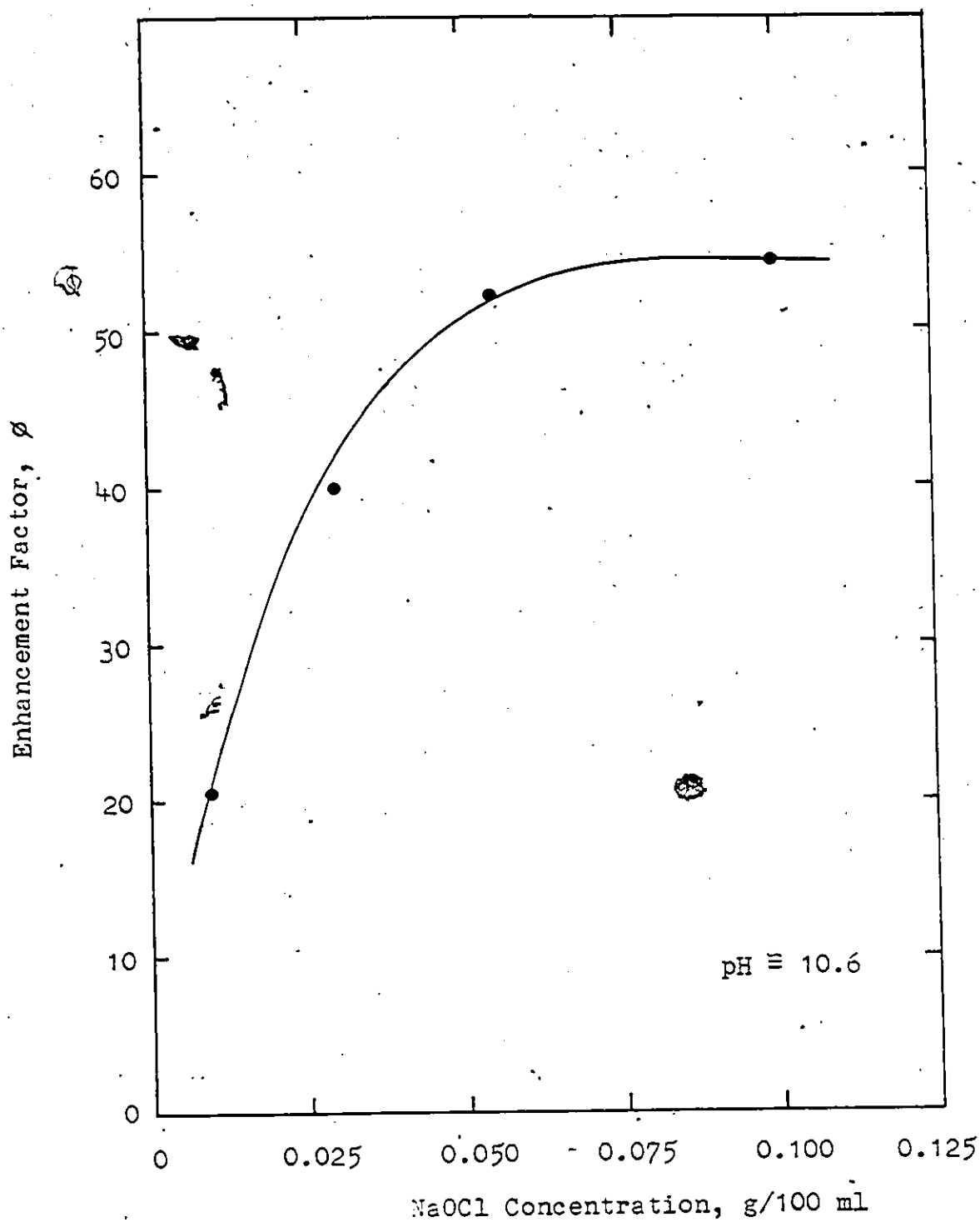


Figure 5-9. Effect of NaOCl Concentration on Enhancement Factor for Scrubbing n-Butyl Mercaptan With Alkaline Sodium Hypochlorite Solutions at 1 atm and 25° C

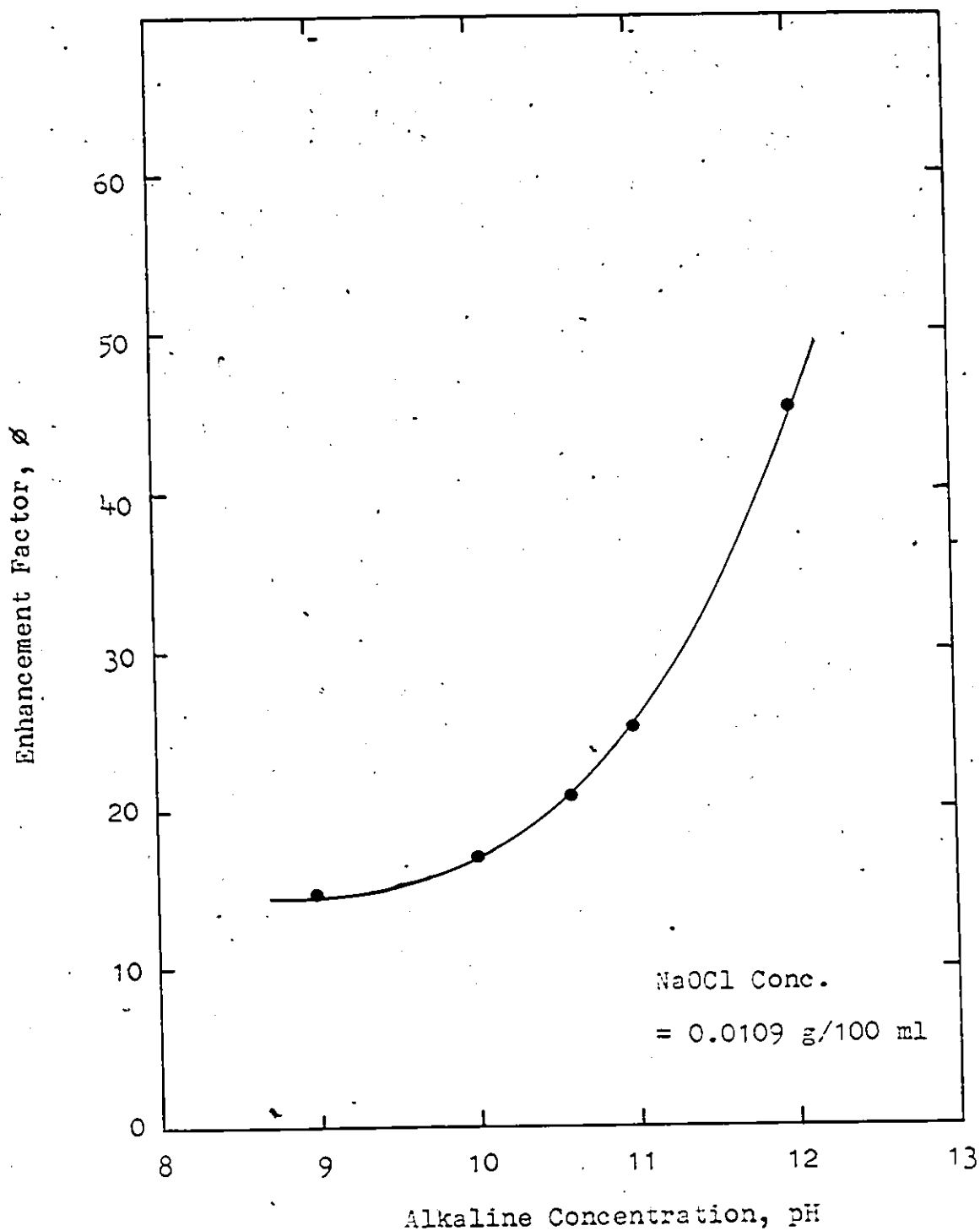


Figure 5-10. Effect of Alkaline Concentration on Enhancement Factor for Scrubbing n-Butyl Mercaptan with Alkaline Sodium Hypochlorite Solutions at 1 atm and 25° C

solubility of n-butyl-mercaptan being much higher at high alkaline concentrations.

Obviously, the reactions occurring in the scrubbing system are complicated. The dissolved n-butyl mercaptan reacts with both hypochlorite and hydroxide ion. Due to the lack of chemical kinetic data, it is not possible to test if the reactions are fast by using Equation 3-31. Alternatively, the enhancement factors obtained experimentally were compared with the enhancement factors for an instantaneous reaction. The enhancement factor for an instantaneous reaction, ϕ_i , can be estimated from the equation given by (22)

$$\phi_i = 1 + \frac{D_B B}{b D_A A_i} \quad (5-5)$$

where

D_A = Diffusivity of the dissolved solute in liquid, ft^2/hr

D_B = Diffusivity of reagent in liquid, ft^2/hr

B = Concentration of reagent in liquid, $\text{lb mole}/\text{ft}^3$

A_i = Concentration of the dissolved solute in liquid at the interface, $\text{lb mole}/\text{ft}^3$

b = Number of moles of reagent reacting with each mole of solute

Assuming $D_A = D_B$, Equation 5-5 becomes

$$\phi_i = 1 + \frac{B}{b A_i} \quad (5-6)$$

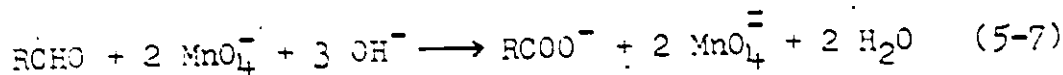
Values of ϕ_1 based on both hypochlorite and hydroxide ion concentrations are listed in Table 5-7. According to Table 5-7, high enhancement factors which are close to the limiting values of ϕ_1 demonstrate that the reactions occurring in the scrubbing system are fast. At low pH (from 9 to 11) the dominant reaction is the oxidation by hypochlorite. When pH exceeds 12, the reaction between n-butyl mercaptan and hydroxide ion becomes dominant.

3. Wet Scrubbing With Alkaline Potassium Permanganate

Solutions

a. Removal of Butyraldehyde

In alkaline permanganate solution, aldehydes are converted to acids according to



The results of scrubbing butyraldehyde with alkaline potassium permanganate solutions are shown in Table 5-8. It was disappointing that poor removal efficiencies were obtained. A higher removal efficiency of butyraldehyde (exceeding 80 %), had been achieved by scrubbing with potassium permanganate solution in Murthy's work ⁽¹⁷⁾. The bubbler scrubber generally has a higher pressure drop relative to the packed bed scrubber and hence is capable of giving a higher removal efficiency. More

NaOCl			NaOH			\bar{y} $\times 10^6$	$A_1 = \bar{y}/\bar{H}_e$ $\times 10^6$	$(\phi_1)_{NaOCl}$	$(\phi_1)_{NaOH}$	ϕ_{actual}
in g/100ml	out	$\bar{E} \times 10^6$	in pH	out pH	$\bar{E} \times 10^6$					
0.0109	0.0013	53.6	9.1	9.3	0.5	117.0	3.40	16.3	1.1	14.2
0.0107	0.0013	51.1	10.1	9.8	5.2	111.0	3.22	16.3	2.8	17.0
0.0103	0.0013	51.1	10.6	10.4	20.1	92.0	2.33	15.2	3.0	20.9
0.0107	0.0012	50.2	11.0	10.3	32.2	105.1	3.05	17.5	11.6	25.2
0.0107	0.0000	49.4	12.0	11.9	546.0	94.5	2.74	19.0	200.4	45.1
0.0109	0.0013	51.1	10.6	10.4	20.1	99.0	2.33	18.7	3.0	20.9
0.0317	0.0224	227.0	10.6	10.3	18.7	95.1	2.74	33.3	7.8	39.9
0.0610	0.0360	406.2	10.7	10.0	13.7	109.0	3.15	130.0	6.9	52.3
0.104	0.0750	749.7	10.6	9.7	14.2	117.5	3.40	220.5	5.2	54.5

Table 5-7. Comparisons of ϕ and ϕ_1 for Scrubbing n-Butyl Mercaptan With Alkaline Sodium Hypochlorite Solutions.

Liquid					Gas			Removal Efficiency %
Flow Rate gpm	Inlet		Outlet		Flow Rate cfm	Inlet Conc. $y \times 10^6$	Outlet Conc. $y \times 10^6$	
	KMnO ₄ g/100ml	pH	KMnO ₄ g/100ml	pH				
1.0	0.030	9.1	0.0297	8.4	20.0	283.3	126.7	55.3
1.0	0.030	10.0	0.0297	9.5	20.0	260.0	113.3	56.4
1.0	0.030	11.0	0.0297	10.8	20.0	214.5	94.5	55.9
1.0	0.030	12.0	0.0294	11.9	20.0	263.3	100.0	62.0
1.0	0.030	11.0	0.0297	10.8	20.0	214.5	94.5	55.9
1.0	0.060	11.0	0.058	10.7	20.0	214.5	90.9	57.6
1.0	0.100	11.0	0.097	10.6	20.0	225.5	90.9	59.7
1.0	0.200	11.0	0.196	10.5	20.0	229.1	87.3	61.9

Table 5-8. Results of Scrubbing Butyraldehyde With Alkaline KMnO₄ Solutions

concentrated potassium permanganate solutions employed in Murthy's tests favored high reductions of butyraldehyde. Posselt and Reidies⁽¹⁵⁾ and Doty et. al.⁽¹⁾ also found poor removal efficiencies when scrubbing aldehydes with potassium permanganate solutions.

The increase in the efficiency of butyraldehyde scrubbing as a result of chemical reaction is again very small. Changes in permanganate concentration along the column are again negligible. Therefore, the rate of oxidation of butyraldehyde by permanganate can also be considered to be very slow as with hypochlorite. The variations of enhancement factor with permanganate and alkaline concentrations are shown in Figures 5-11 and 5-12. An increase in permanganate concentration has a slightly beneficial effect on the enhancement factor through an increased rate of reaction. The influence of alkaline concentration on the enhancement factor is very slight, but the increase of enhancement factor with increasing pH is obvious. This is inconsistent with Murthy's results⁽¹⁷⁾ which show a negative effect of pH on the rate of absorption of isovaleraldehyde. It is conceivable that the isovaleraldehyde hydrate formed when the aldehyde dissolves in water can not be oxidized faster than the normal isovaleraldehyde. An increase in alkaline concentration will increase the formation of isovaleraldehyde hydrate, but will decrease the oxidative power of permanganate.

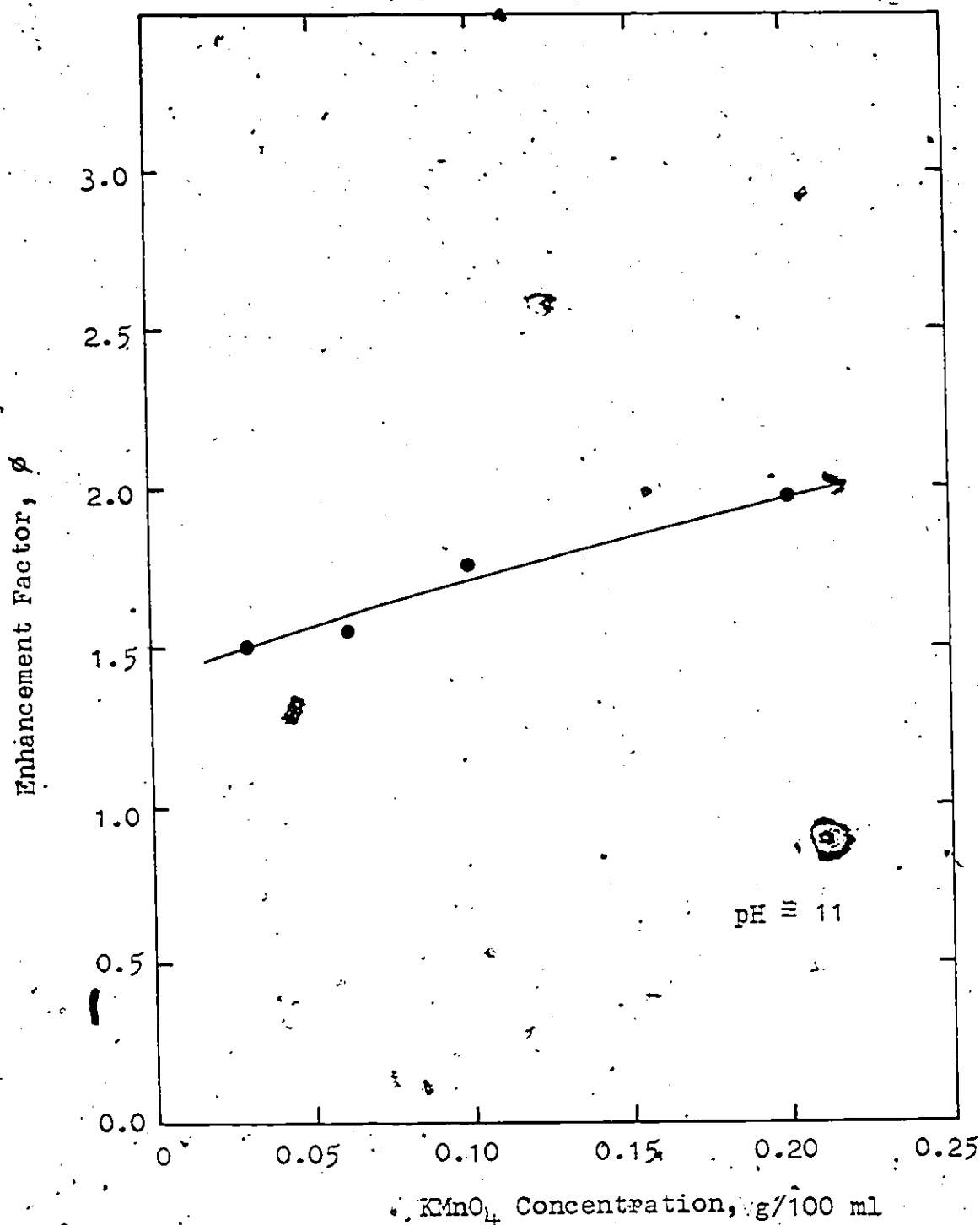


Figure 5.11. Effect of KMnO₄ Concentration on Enhancement Factor for Scrubbing Butyraldehyde With Alkaline Potassium Permanganate Solutions at 1 atm and 25°C

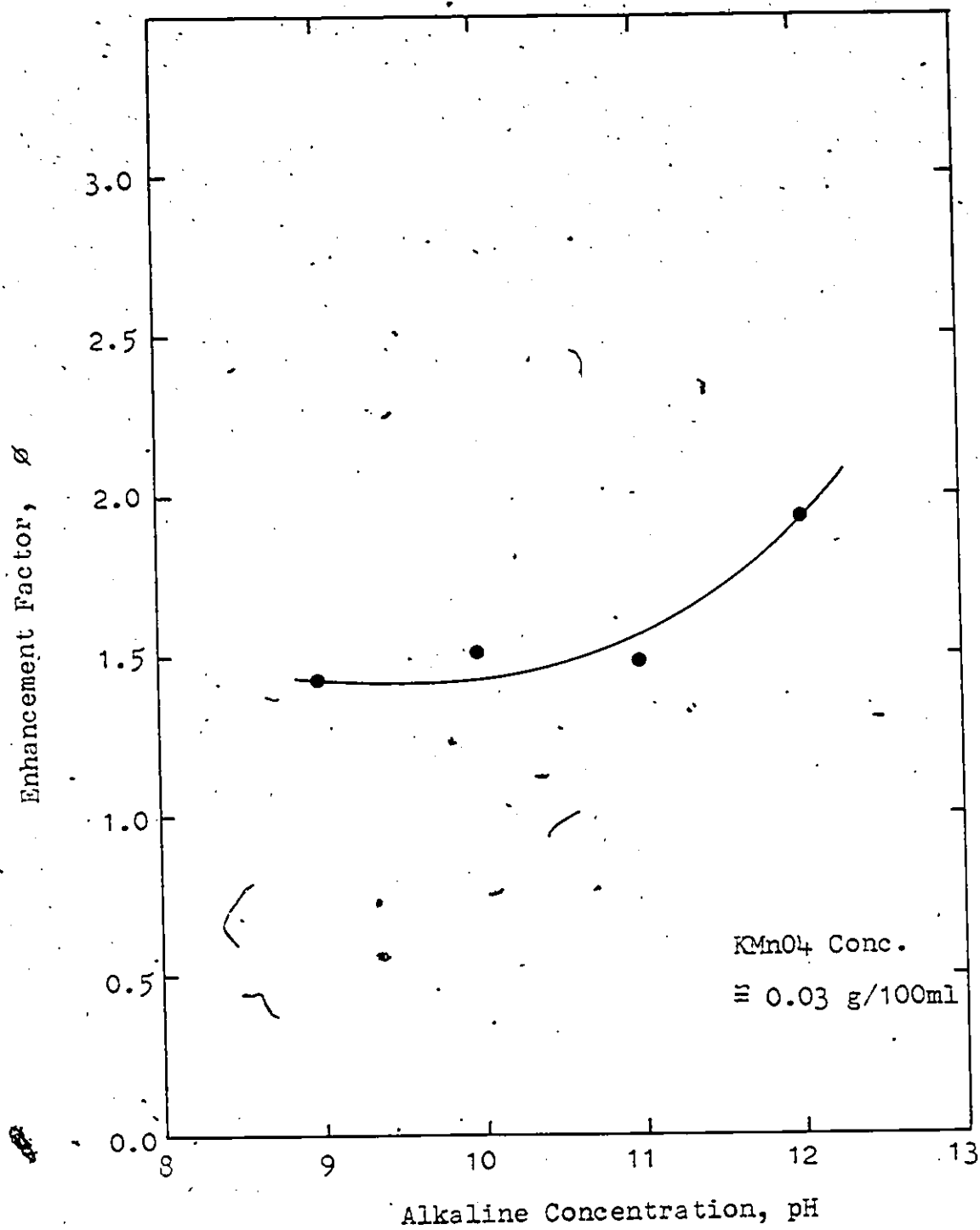


Figure 5-12. Effect of Alkaline Concentration on Enhancement Factor for Scrubbing Butyraldehyde With Alkaline Potassium Permanganate Solutions at 1 atm and 25° C

b. Removal of n-Butyl Mercaptan

When mercaptans are absorbed by alkaline potassium permanganate solution, the following reactions can occur:



The results of scrubbing n-butyl mercaptan with alkaline potassium permanganate solutions are shown in Table 5-9. High odor removal efficiencies were obtained. This implies that the reactions occurring during the scrubbing process are fast. The influence of permanganate and alkaline concentrations on the enhancement factor is shown in Figures 5-13 and 5-14 respectively. The enhancement factor is highly affected by the permanganate concentration. An increase in KMnO_4 concentration will enhance the reaction rate and, hence, increase the enhancement factor. The enhancement factor is also increased by increasing the alkaline concentration. The curve is similar to that obtained during scrubbing with sodium hypochlorite solutions. The enhancement factor increases slowly at low pH values (from 9 to 11) but changes dramatically when the pH exceeds 11. Positive effects of KMnO_4 and pH of the solution on the rate of mercaptan removal were also found by Murthy (17).

Liquid					Gas			Removal Efficiency %
Flow Rate gpm.	Inlet		Outlet		Flow Rate cfm	Inlet Conc. $y \times 10^6$	Outlet Conc. $y \times 10^6$	
	KMnO ₄ g/100ml	pH	KMnO ₄ g/100ml	pH				
0.5	0.030	9.1	0.024	8.6	20.0	168	126	25.0
0.5	0.030	10.1	0.022	9.8	20.0	156	102	34.6
0.5	0.030	11.0	0.015	10.8	20.0	153	57	62.7
0.5	0.030	12.0	0.000	12.0	20.0	150	16.5	89.0
0.5	0.030	11.0	0.015	10.8	20.0	153	57	62.7
0.5	0.060	11.0	0.040	10.8	20.0	174	39	77.6
0.5	0.10	11.1	0.077	10.9	20.0	168	27	83.9
0.5	0.20	11.1	0.176	10.9	20.0	174	12	93.1

Table 5-9. Results of Scrubbing n-Butyl Mercaptan With Alkaline KMnO₄ Solutions

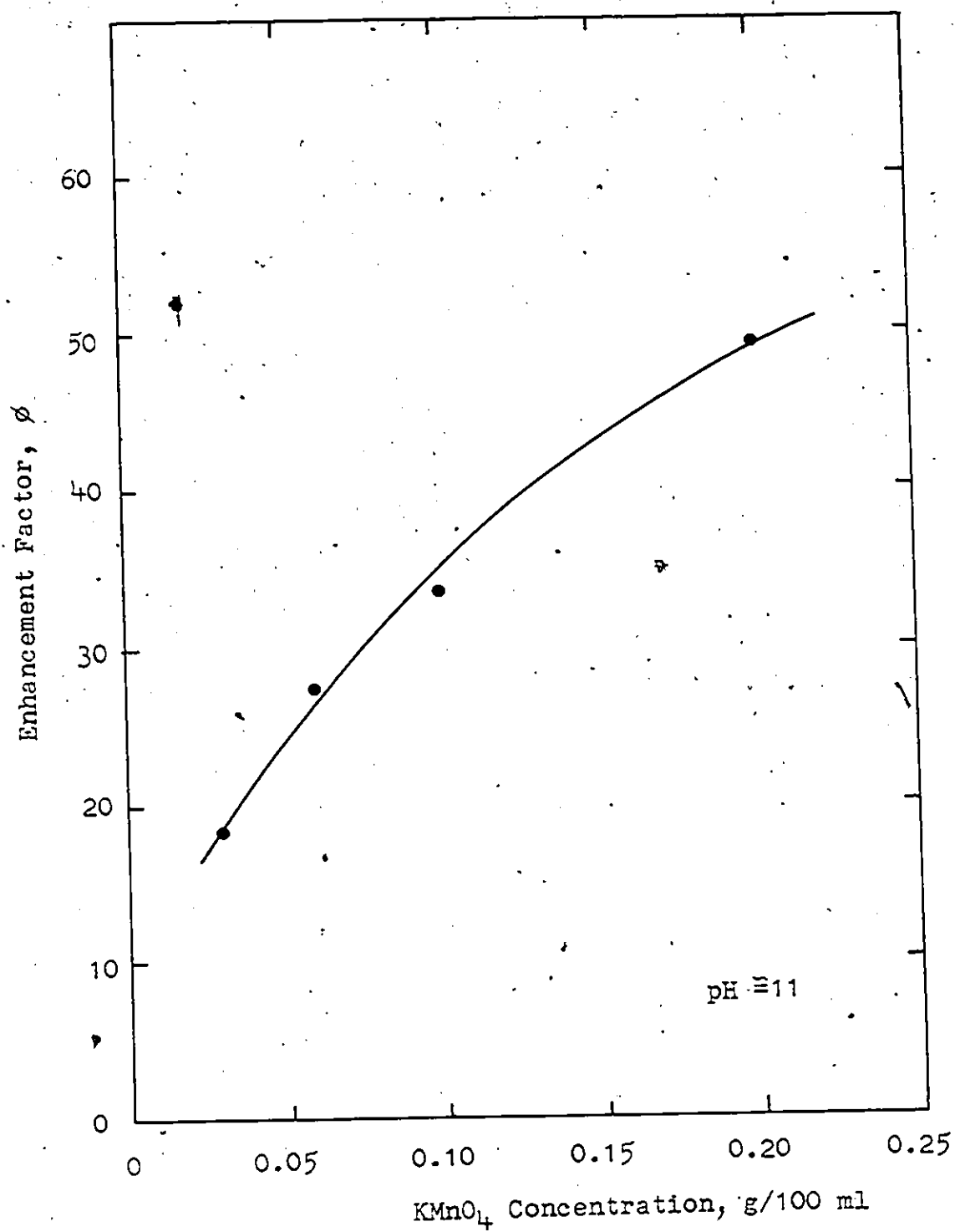


Figure 5-13. Effect of KMnO₄ Concentration on Enhancement Factor for Scrubbing n-Butyl Mercaptan with Alkaline Potassium Permanganate Solutions at 1 atm and 25° C

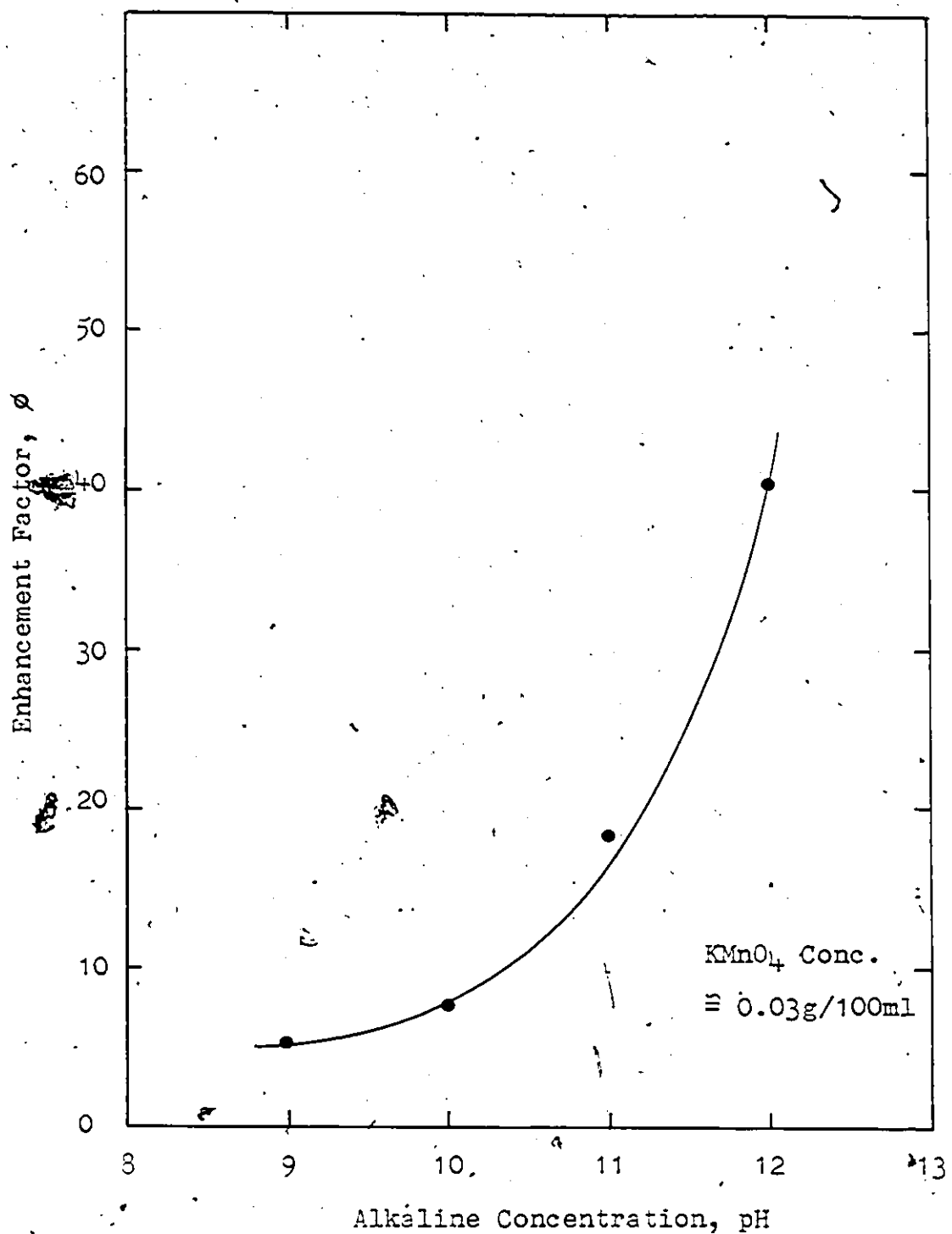


Figure 5-14. Effect of Alkaline Concentration on Enhancement Factor for Scrubbing n-Butyl Mercaptan with Alkaline Potassium Permanganate Solutions at 1 atm and 25° C

Since the reaction rate and mechanism are still obscure, testing of the criterion for a fast reaction as described by Equation 3-31 is again not feasible. Comparisons of the experimental enhancement factors with the enhancement factors for an instantaneous reaction are tabulated in Table 5-10. High enhancement factors approaching the limiting values of β_1 again demonstrate that the reactions occurring in the scrubbing process are fast. As in the hypochlorite scrubbing system the oxidant reaction is dominant at low pH but the reaction with hydroxide ion becomes important at high pH.

C. Scrubber Design Considerations of Oxidant and Alkaline Concentrations

The oxidant concentrations considered here ranged from 0.01 to 0.20 % by weight. For butyraldehyde scrubbing, a further increase in oxidant concentration (above 0.20 %) should lead to a higher odor removal due to the increased reaction rate. This positive effect of oxidant concentration on the removal efficiency is very slight when scrubbing n-butyl mercaptan, as illustrated by Figure 5-9, because the gas-side mass transfer resistance becomes controlling. From a plant operation point of view (eg. corrosion behavior), it is desirable to select pH values of scrubbing solutions in the range of 9 to 12.

KMnO ₄		NaOH			\bar{y} *10 ⁶	$A_1 = \bar{y}/H_e$ *10 ⁶	$(\phi_1)_{KMnO_4}$	$(\phi_1)_{NaOH}$	ϕ_{actual}
in g/100ml	out g/100ml	$\bar{B} * 10^6$	in pH	out pH					
0.030	0.024	106.6	9.1	8.6	0.5	147.0	26.0	1.1	5.3
0.030	0.022	102.7	10.1	9.8	5.9	129.0	28.5	2.6	7.8
0.030	0.018	88.8	11.0	10.8	51.0	105.0	30.1	17.7	18.2
0.030	0.000	59.2	12.0	12.0	624.0	83.0	25.3	261.7	40.6
0.030	0.013	88.8	11.0	10.8	51.0	105.0	30.1	17.7	18.2
0.060	0.040	197.5	11.0	10.8	51.0	106.5	64.9	17.5	27.5
0.10	0.077	349.6	11.0	10.9	64.1	97.5	125.4	23.8	33.6
0.20	0.176	742.7	11.0	10.9	64.1	93.0	276.0	24.7	49.2

Table 5-10. Comparisons of ϕ and ϕ_1 for Scrubbing n-Butyl Mercaptan With Alkaline potassium Permanganate Solutions

Cost comparisons of alkaline sodium hypochlorite and alkaline potassium permanganate solutions used in scrubbing of butyraldehyde and n-butyl mercaptan are shown in Figures 5-15 to 5-18 where the cost required per unit increase in the enhancement factor is plotted against oxidant and alkaline concentrations. The costs of potassium permanganate, sodium hypochlorite and sodium hydroxide are based on the 1977 prices quoted by Lawrason Chemical Company⁽³⁰⁾ as shown in Table 5-11. Figures 5-16 and 5-18 indicate that cost/ $(\phi - 1)$ decreases with increasing alkaline concentration over the test range. Although an increase in oxidant concentration is also beneficial, it will increase the cost required per unit increase in the enhancement factor as shown in Figures 5-15 and 5-17. Therefore, from an economical point of view, it is preferable to operate at high alkaline concentrations, about pH 12, rather than to use high oxidant concentrations. According to Figure 5-15 the removal of butyraldehyde by wet scrubbing with alkaline potassium permanganate solution is slightly more economical than with alkaline sodium hypochlorite solution. On the other hand, the removal of n-butyl mercaptan is much cheaper with alkaline sodium hypochlorite than with alkaline potassium permanganate as indicated by Figure 5-17.

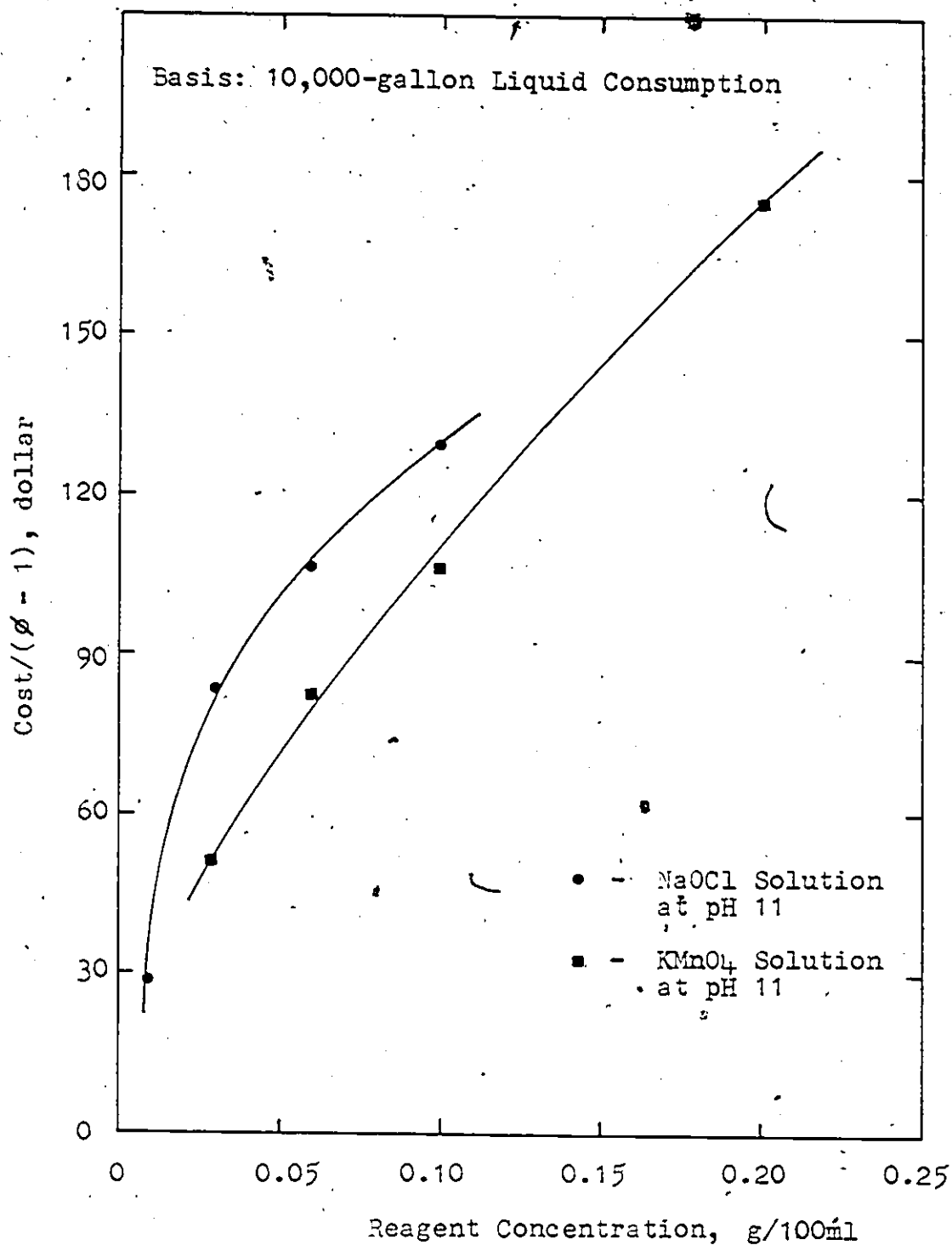


Figure 5-15. Cost Comparisons Between NaOCl and KMnO₄ Solutions for Scrubbing Butyraldehyde with Varying Reagent Concentrations

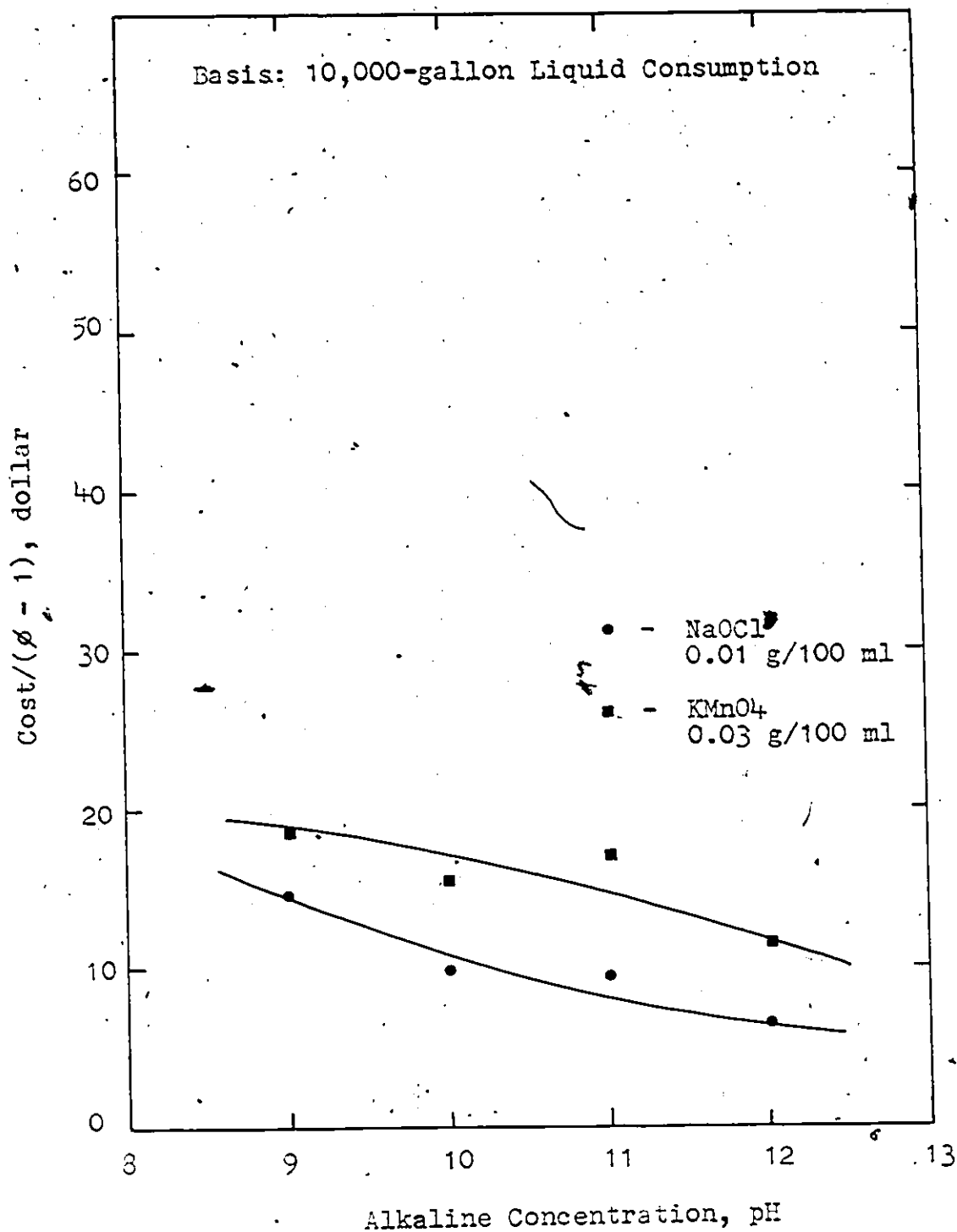


Figure 5-16. Cost Comparisons Between NaOCl and KMnO₄ Solutions for Scrubbing Butyraldehyde with Varying Alkaline Concentrations

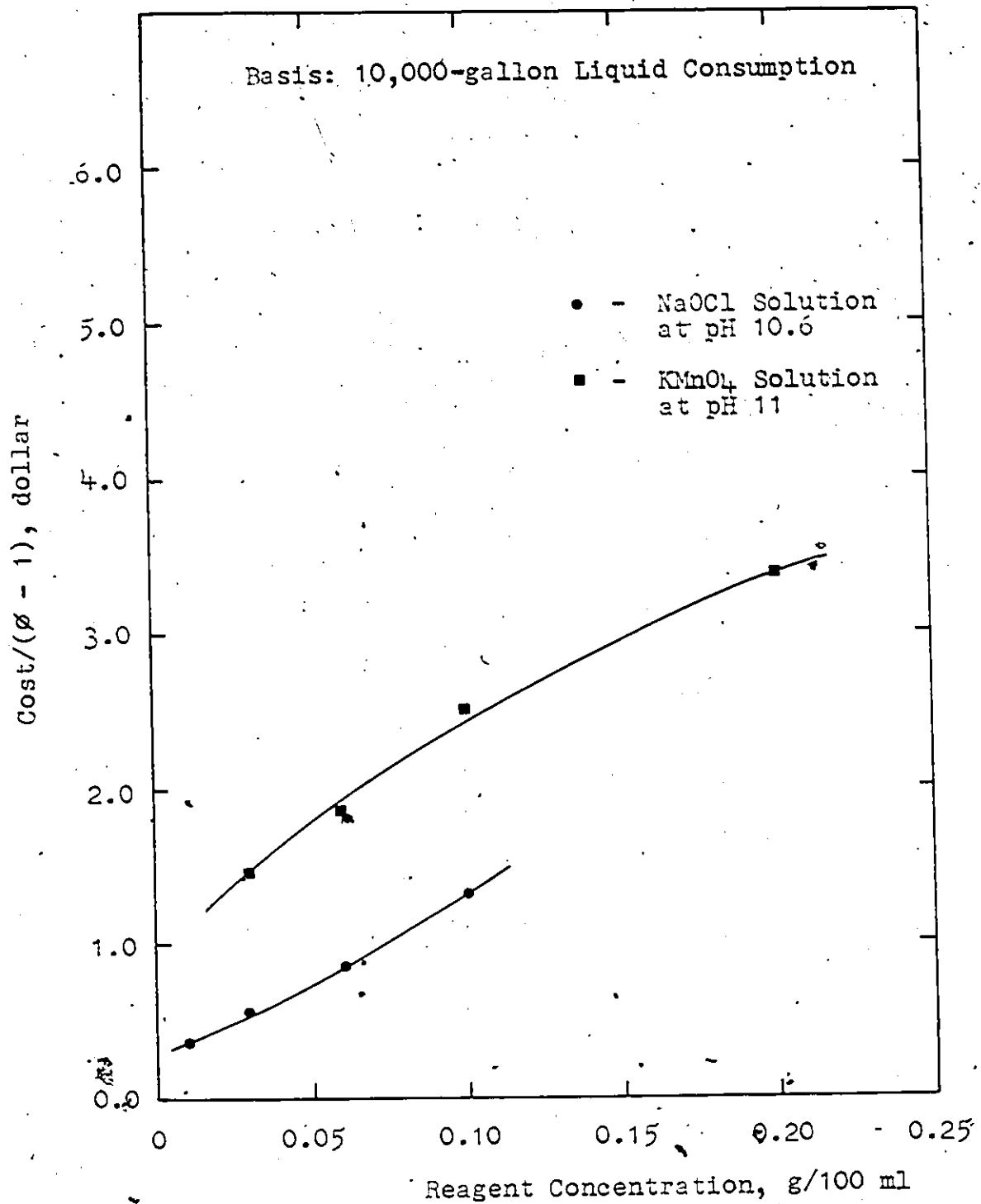


Figure 5-17. Cost Comparisons Between NaOCl and KMnO₄ Solutions for Scrubbing n-Butyl Mercaptan with Varying Reagent Concentrations

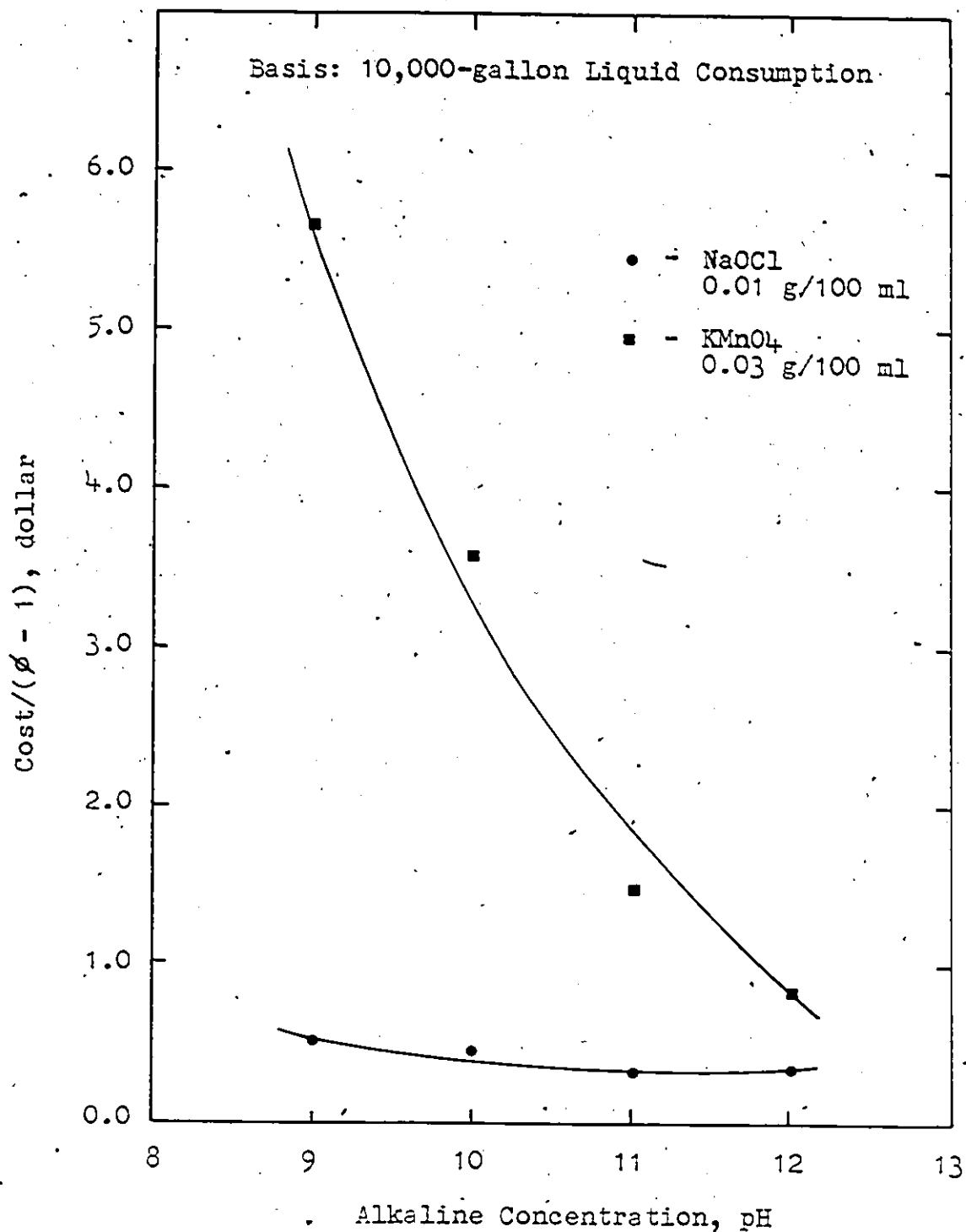


Figure 5-18. Cost Comparisons Between NaOCl and KMnO₄ Solutions for Scrubbing n-Butyl Mercaptan with Varying Alkaline Concentrations

Reagent	Price
KMnO ₄ solid, technical grade, 110-pound package	\$ 0.97/lb
NaOCl, 16% solution, technical grade	\$ 5.60/gal
NaOH, flake, technical grade	\$ 0.23/lb

Table 5-11. Costs of Chemical Reagents Based on 1977 Prices (30)

VI. CONCLUSIONS

1. Both gaseous butyraldehyde and n-butyl mercaptan dissolve in water according to Henry's law under the test conditions. Gaseous butyraldehyde is slightly soluble in water, but n-butyl mercaptan is almost completely insoluble.
2. The overall gas-side mass transfer coefficients are independent of the gas flow rate. As a result, the gas-side mass transfer resistance can be eliminated. The rate of absorption is controlled by the liquid-side mass transfer resistance for both butyraldehyde and n-butyl mercaptan scrubbing systems.
3. Both alkaline sodium hypochlorite and alkaline potassium permanganate solutions can provide high enhancement factors for scrubbing n-butyl mercaptan but give poor efficiencies for butyraldehyde removal.
4. Both hypochlorite and permanganate concentrations have positive effects on the enhancement factor for butyraldehyde and n-butyl mercaptan removal. An increase in enhancement factor with increasing alkalinity of hypochlorite and permanganate solutions is also found for both odorous compounds.

5. Cost comparisons indicate that alkaline permanganate solution is slightly more economical for butyraldehyde removal, but alkaline hypochlorite solution is much cheaper when scrubbing n-butyl mercaptan. From an economical point of view, it is preferable to operate at high alkaline concentrations, about pH 12, rather than to increase the oxidant concentrations.

NOMENCLATURE

a	Interfacial area per unit of packed volume, ft^{-1}
A	Concentration of dissolved solute in the bulk of the liquid, lb mole/ft^3
A_i	Concentration of dissolved solute at the interface, lb mole/ft^3
B	Concentration of reagent in liquid, lb mole/ft^3
C_i	Concentration of ion in the solution, gmole/l
D_A	Diffusivity of the dissolved solute in liquid, ft^2/hr
D_B	Diffusivity of reagent in liquid, ft^2/hr
G	Gas mass flux, $\text{lb}/(\text{ft}^2)(\text{hr})$
G_m	Gas molar flux, $\text{lb mole}/(\text{ft}^2)(\text{hr})$
h	Salting-out parameter, l/gmole
h_a	Contribution of anion to h , l/gmole
h_c	Contribution of cation to h , l/gmole
h_g	Contribution of gas to h , l/gmole
H_e	Henry's law constant, mole fraction/mole fraction
H_e'	Henry's law constant, mm Hg/mole fraction
H_e^o	Henry's law constant for water system, mole fraction/mole fraction
I	Ionic strength
k_1	Rate constant for the first-order reaction, s^{-1}
k_2	Rate constant for the second-order reaction, $\text{ft}^3/(\text{lb mole})(\text{s})$

NOMENCLATURE (cont.)

k_g	Gas-side mass transfer coefficient, lb mole/(ft ²)(hr)
k'_g	Gas-side mass transfer coefficient, lb mole/(ft ²)(hr)(atm)
K_G	Overall gas-side mass transfer coefficient, lb mole/(ft ²)(hr)
K_{GR}	Defined by Equation 3-23
k_l	Liquid-side mass transfer coefficient, lb mole/(ft ²)(hr)
k'_l	Liquid-side mass transfer coefficient, ft/hr
K_L	Overall liquid-side mass transfer coefficient, lb mole/(ft ²)(hr)
L	Liquid mass flux, lb/(ft ²)(hr)
L_m	Liquid molar flux, lb mole/(ft ²)(hr)
N	Mass transfer flux of solute, lb mole/(ft ²)(hr)
p	Partial pressure of the solute, atm or mm Hg
p_i	Partial pressure of the solute at the interface, atm
P	Total pressure, atm
r	Rate of reaction, lb mole/(ft ³)(s)
S	Slope of the operating line, defined by Equation 3-19
x	Mole fraction of the dissolved solute in liquid
x_i	Mole fraction of the dissolved solute in liquid at the interface
x^*	Mole fraction of the dissolved solute in liquid, defined by Equation 3-13
y	Mole fraction of solute in the gas

NOMENCLATURE (cont.)

y_i	Mole fraction of solute in the gas at the interface
y^*	Mole fraction of solute in the gas, defined by Equation 3-12 .
z	Height of the packed bed, ft
Z	Total height of the packed bed, ft
z_i	Valence of ion

Greek Symbols

μ_L	Viscosity of liquid, lb/(ft)(hr)
ρ_L	Density of liquid, lb/ft ³
$\bar{\rho}_L$	Average molar density of liquid, lb mole/ft ³
ϕ	Enhancement factor, defined by Equations 3-32 and 3-33
ϕ_i	Defined by Equation 5-5

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APPENDIX I

Error Analysis

A. Solubility Measurements

The major source of error in solubility measurements is the determination of odorant concentrations. Sampling volumes and injecting technique are two important factors responsible for errors in gas chromatographic analysis. In the determination of odorant concentrations, each sample had been injected into the gas chromatograph three times. A typical result of three different injections of the same sample is shown in Figure I-1. Reproducibility of the G. C. results of all of the experiments was within $\pm 2.5\%$.

B. Wet Scrubbing Measurements

The possible sources of error associated with wet scrubbing measurements are:

- i. air temperature and pressure variations,
- ii. liquid temperature variations,
- iii. gas and liquid flow rate variations,
- iv. oxidant and alkaline concentration variations,
- v. sampling technique,
- vi. G. C. accuracy.

The results of replicate runs for scrubbing n-butyl mercaptan with alkaline potassium permanganate solutions are listed in Table I-1. The reproducibility of replicate runs was found to be within $\pm 5.1\%$. This represents very good agreement between

Odorant: n-Butyl Mercaptan, 53.6 ppm
Oven temperature: 125° C.
Detector temperature: 150° C.
Injector temperature: 150° C.

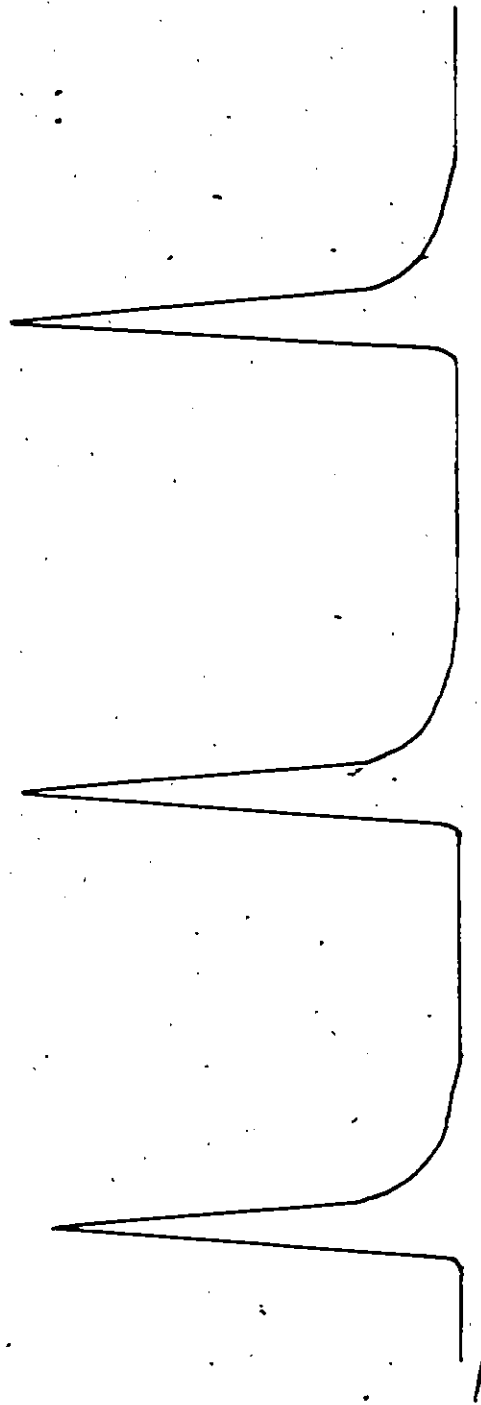


Figure 1-1. Results of Three Different Injections of Same Sample into
Gas Chromatograph

KMnO ₄ Conc. g/100 ml	First Runs			Replicate Runs			Absolute Difference in Percent Removal Efficiency
	Odor Conc. y * 10 ⁶		Removal Efficiency %	Odor Conc. y * 10 ⁶		Removal Efficiency	
	Inlet	Outlet		Inlet	Outlet		
0.030	153.0	57.0	62.7	143.3	53.0	59.5	5.1
0.060	174.0	39.0	77.6	159.1	35.0	73.0	0.5
0.10	163.0	27.0	33.9	159.2	23.0	35.6	2.0
0.20	174.0	12.0	93.1	175.5	12.5	92.9	0.2

Gas Flow Rate: 20.0 cfm

Liquid Flowrate: 0.5 gpm

pH of the Solutions: 11

Table I-1. Results of Replicate Runs for Scrubbing n-Butyl Mercaptan With Alkaline Potassium Permanganate Solutions

data obtained during different time periods in the overall program. The replication was carried out 5 months after the original data acquisition using new batches of odorant and scrubbing liquid.

APPENDIX II

Measurement of The Vapor Pressure of Butyraldehyde

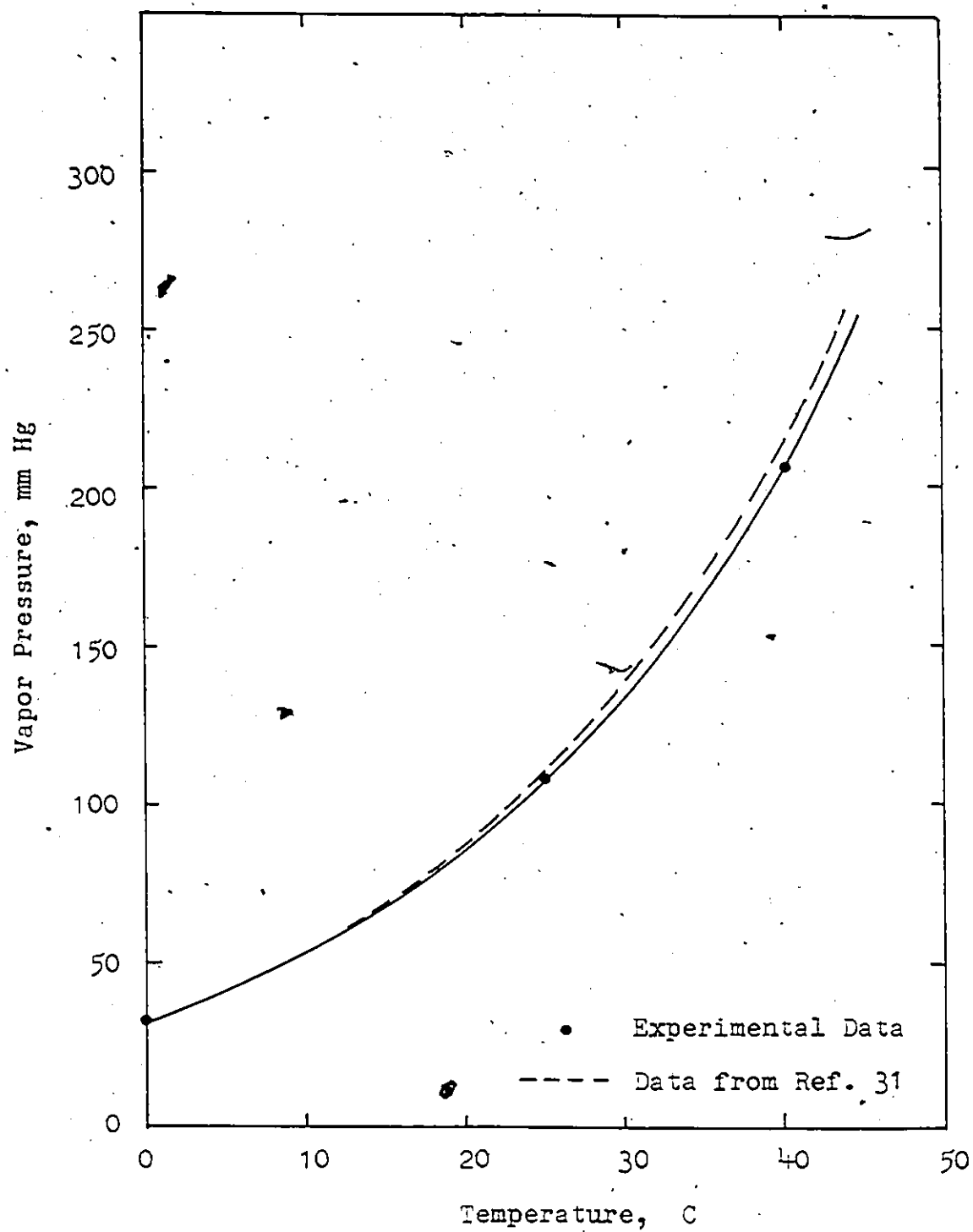


Figure-II-1. The Vapor Pressure of Butyraldehyde at 1 atm

APPENDIX III

Evaluation of Henry's Law Constants

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas $y \times 10^6$	Solute Conc. in Liquid, x			Henry's Law Constant
				Micro- Liter	$\times 10^6$ mole		$x_{calc.}$ $\times 10^6$	$x_{meas.}$ $\times 10^6$	Diff. %	
0	1	10	660	7.0	79.1	134.3	135.2	121.7	+ 11.1	1.11
	2	20	650	7.0	79.1	73.3	69.1	66.7	+ 3.6	1.17
	3	30	970	7.0	79.1	56.5	46.0	48.3	- 4.8	1.17
	4	40	1560	8.0	90.4	43.5	39.3	35.0	+12.3	1.24
25										Ave. 1.17
	1	30	990	4.0	45.2	215.6	21.38	23.45	- 6.7	9.19
	2	50	970	4.0	45.2	133.3	14.36	14.14	+ 1.6	9.43
	3	75	945	4.0	45.2	97.8	9.94	10.00	- 0.6	9.73
	4	100	920	4.0	45.2	75.6	7.62	7.59	+ 0.4	9.96
	5	30	640	4.0	45.2	226.7	23.58	24.14	- 2.3	9.39
	6	50	620	4.0	45.2	146.7	14.94	14.43	+ 3.2	10.13
	7	75	925	4.0	45.2	97.8	9.96	9.66	+ 3.1	10.12
	8	100	1500	4.0	45.2	68.9	7.38	7.59	- 2.8	9.08
										Ave. 9.64

Table III-1. Solubility of Butyraldehyde in Water at 1 atm

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas $y \times 10^6$	Solute Conc. in Liquid, x			Henry's Law Constant
				Micro- Liter	$\times 10^6$ mole		x calc. $\times 10^6$	x meas. $\times 10^6$	Diff. $\frac{y}{x}$	
40	1	80	420	3.0	33.9	148.9	7.10	6.90	+ 2.9	21.53
	2	120	900	3.0	33.9	108.9	4.53	4.83	- 6.2	22.55
	3	160	860	3.0	33.9	77.3	3.53	3.66	- 3.6	21.25
	4	200	820	3.0	33.9	64.4	2.87	2.93	- 2.0	21.98
	5	50	450	3.0	33.9	226.7	10.77	10.52	+ 2.4	21.55
	6	75	945	3.0	33.9	142.2	6.88	7.07	- 2.7	20.11
	7	100	920	3.0	33.9	122.2	5.31	5.69	- 6.7	21.47
	8	125	895	3.0	33.9	95.6	4.40	4.31	+ 2.1	22.13
										Ave. 21.53

Table III-1. Solubility of Butyraldehyde in Water at 1 atm (cont.)

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas $y \times 10^6$	Solute Conc. in Liquid, x			Henry's Law Constant
				Micro- Liter	$\times 10^6$ mole		x calc. $\times 10^6$	x meas. $\times 10^6$	Diff. $\frac{x}{y}$	
0	1	80	1520	3.0	28.0	1198	3.28	3.34	- 1.8	59.3
	2	60	940	3.0	28.0	294	4.70	4.94	- 4.9	59.5
	3	50	970	3.0	28.0	316	5.15	5.12	+ 0.6	61.7
	4	35	635	3.0	28.0	470	7.55	7.66	- 1.4	61.4
										Ave. 60.5
25	1	100	900	2.5	23.34	263	2.43	2.28	+ 6.6	117.5
	2	80	1520	2.5	23.34	244	1.83	1.97	- 7.1	123.9
	3	90	940	2.5	23.34	323	2.46	2.69	- 8.6	120.1
	4	60	1440	2.5	23.34	506	4.27	4.46	- 4.3	113.5
	5	60	960	2.5	23.34	324	3.19	2.76	+15.6	117.4
	6	40	980	2.5	23.34	403	3.23	3.50	- 7.7	115.1
	7	30	640	2.5	23.34	563	5.16	4.8	- 7.5	117.3
	8	30	640	2.5	23.34	569	5.06	4.32	-14.6	131.7
										Ave. 120.0

Table III-2. Solubility of n-Butyl Mercaptan in Water at 1 atm

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas $y \times 10^6$	Solute Conc. in Liquid, x			Henry's Law Constant
				Micro- Liter	$\times 10^6$ mole		$x_{calc.} \times 10^6$	$x_{meas.} \times 10^6$	Diff, %	
40	1	100	920	2.0	13.67	326	1.25	1.14	+ 9.6	235
	2	100	920	2.0	13.67	336	1.19	1.16	+ 2.5	290
	3	30	940	2.0	13.67	343	1.33	1.19	+11.3	292
	4	30	470	1.5	14.00	569	2.15	2.17	+ 0.9	262
										Ave. 232

Table III-2. Solubility of nButyl Mercaptan in Water at 1 atm (cont.)

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas, y $\times 10^6$	Solute Conc. in Liquid, x $\times 10^6$	Henry's Law Constant
				Micro- Liter	$\times 10^6$ mole			
0	1	10	1010	8.0	90.4	226.1	144.4	1.57
	2	20	1000	8.0	90.4	126.1	76.35	1.65
	3	30	990	8.0	90.4	37.0	51.93	1.68
	4	40	980	8.0	90.4	69.6	39.31	1.77
								Ave. 1.67
25	1	40	980	4.0	45.2	222.2	16.33	13.59
	2	70	950	4.0	45.2	142.2	10.20	13.94
	3	100	920	4.0	45.2	102.2	7.44	13.74
	4	120	900	4.0	45.2	86.7	6.30	13.76
	5	140	630	4.0	45.2	244.4	17.51	13.96
	6	60	610	4.0	45.2	163.9	12.30	13.73
	7	30	920	4.0	45.2	116.1	9.19	12.63
	8	120	1430	4.0	45.2	34.4	6.01	14.00
								Ave. 13.67

Table III-3.. Solubility of Butyraldehyde in 1 M NaCl Solution at 1 atm

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas $\frac{y}{x}$ * 10	Solute Conc. in Liquid, x * 10	Henry's Law Constant
				Micro- Liter	*10 ⁶ mole			
40	1	50	450	3.0	33.9	308.7	10.26	30.08
	2	75	945	3.0	33.9	197.8	6.39	30.95
	3	100	920	3.0	33.9	154.3	5.11	30.20
	4	125	895	3.0	33.9	130.4	4.23	30.83
								Ave. 30.52

Table III-3. Solubility of Butyraldehyde in 1 M NaCl Solution at 1 atm (cont.)

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas, y $\times 10^6$	Solute Conc. in Liquid, x $\times 10$	Henry's Law Constant
				Micro- Liter	$\times 10^6$ mole			
0	1	100	1500	1.5	14.0	122	1.05	116
	2	80	940	2.5	23.34	305	2.37	129
	3	60	960	2.5	23.34	326	2.81	116
	4	50	970	2.5	23.34	345	3.02	114
								Ave. 119
25	1	100	1500	2.0	18.67	209	1.05	199
	2	80	920	2.0	18.67	319	1.50	213
	3	80	940	2.0	18.67	305	1.56	196
	4	50	970	2.0	18.67	357	1.62	220
	5	50	620	2.0	18.67	245	1.12	219
	6	25	645	2.0	18.67	286	1.29	222
								Ave. 212

Table III-4. Solubility of n-Butyl Mercaptan in 1 M NaCl Solution at 1 atm

Temp. °C	Run#	Liquid Volume ml	Gas Volume ml	Liquid Solute Injected		Solute Conc. in Gas, y * 10 ⁶	Solute Conc. in Liquid, x * 10 ⁶	Henry's Law Constant
				Micro- Liter	*10 ⁶ mole			
40	1	120	900	1.5	14.0	282	0.62	455
	2	80	940	1.5	14.0	303	0.65	466
	3	50	970	1.5	14.0	321	0.68	472
	4	40	630	1.5	14.0	476	1.05	456
								Ave. 462

Table III-4. Solubility of n-Butyl Mercaptan in 1 M NaCl Solution at 1 atm (cont.)

APPENDIX IV

Calculations of Mass Transfer Coefficients

The sample calculations presented here involve typical rationalization of the mass transfer data acquired during this program. All experiments were carried out at 1 atm and about 25° C in a 6" I.D. scrubber packed to a 2.8 foot height with 5/8" stainless steel Pall rings.

A. Wet Scrubbing With Water

1. Butyraldehyde Removal

Data: Gas: Flow rate: 20 cfm (Table 5-2)
 Inlet odor conc., y_B : 206.3×10^{-6} (Table 5-2)
 Outlet odor conc., y_T : 110.4×10^{-6} (Table 5-2)
 Henry's law constant: 9.64 (Figure 5-1)
 Liquid: Flow rate: 1.0 gpm (Table 5-2)

Calculations:

Mass flux:

$$G = \frac{(20 \text{ cfm})(0.075 \text{ lb/ft}^3)(60 \text{ min/hr})}{0.2 \text{ ft}^2} = 450 \text{ lb/ft}^2(\text{hr})$$

$$L = \frac{(1.0 \text{ gpm})(8.34 \text{ lb/gal})(60 \text{ min/hr})}{0.2 \text{ ft}^2} = 2500 \text{ lb/ft}^2(\text{hr})$$

Molar flux:

$$G_m = \frac{450 \text{ lb/ft}^2(\text{hr})}{29 \text{ lb/lb mole}} = 15.5 \text{ lb mole/ft}^2(\text{hr})$$

$$L_m = \frac{2500 \text{ lb/ft}^2(\text{hr})}{18 \text{ lb/lb mole}} = 138.9 \text{ lb mole/ft}^2(\text{hr})$$

Overall gas-side mass transfer coefficient:

From Equations 3-13 and 3-19

$$S = \frac{(9.64)(15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr}))}{138.9 \text{ lb mole}/(\text{ft}^2)(\text{hr})} = 1.076$$

$$K_{Ga} = \frac{15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{(2.8 \text{ ft})(1 - 1.076)} \ln((1 - 1.076) \left(\frac{206.3 \times 10^{-6}}{110.4 \times 10^{-6}} \right) + 1.076) = 4.97 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Liquid-side mass transfer coefficient:

Neglecting the gas-side mass transfer resistance,

Equation 3-10 yields

$$k_{La} = (K_{Ga})(H_e) = (4.97 \text{ lb mole}/(\text{ft}^3)(\text{hr}))(9.64) \\ = 47.9 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

2. n-Butyl Mercaptan Removal

Data:	Gas	Flow rate:	20 cfm	(Table 5-3)
		Inlet odor conc., y_B :	169.1×10^{-6}	(Table 5-3)
		Outlet odor conc., y_T :	164.3×10^{-6}	(Table 5-3)
		Henry's law constant:	120	(Figure 5-2)
	Liquid:	Flow rate:	0.5 gpm	(Table 5-3)

Calculations:

Mass flux:

$$G = \frac{(20 \text{ cfm})(0.075 \text{ lb}/\text{ft}^3)(60 \text{ min}/\text{hr})}{0.2 \text{ ft}^2} = 450 \text{ lb}/(\text{ft}^2)(\text{hr})$$

$$L = \frac{(0.5 \text{ gpm})(8.34 \text{ lb/gal})(60 \text{ min/hr})}{0.2 \text{ ft}^2} = 1250 \text{ lb/ft}^2(\text{hr})$$

Molar flux:

$$G_m = \frac{450 \text{ lb/ft}^2(\text{hr})}{29 \text{ lb/lb mole}} = 15.5 \text{ lb mole/ft}^2(\text{hr})$$

$$L_m = \frac{1250 \text{ lb/ft}^2(\text{hr})}{18 \text{ lb/lb mole}} = 69.4 \text{ lb mole/ft}^2(\text{hr})$$

Overall gas-side mass transfer coefficient:

From Equations 3-18 and 3-19

$$S = \frac{(120)(15.5 \text{ lb mole/ft}^2(\text{hr}))}{69.4 \text{ lb mole/ft}^2(\text{hr})} = 26.8$$

$$K_{Ga} = \frac{15.5 \text{ lb mole/ft}^2(\text{hr})}{(2.8 \text{ ft})(1 - 26.8)} \ln\left((1 - 26.8)\left(\frac{169.1 \times 10^{-6}}{164.3 \times 10^{-6}}\right) + 26.8\right) = 0.3 \text{ lb mole/ft}^3(\text{hr})$$

Liquid-side mass transfer coefficient:

Neglecting the gas-side mass transfer resistance,

Equation 3-10 gives

$$k_L a = (K_{Ga})(H_e) = (0.3 \text{ lb mole/ft}^3(\text{hr}))(120) = 36.0 \text{ lb mole/ft}^3(\text{hr})$$

B. Wet Scrubbing With Alkaline Sodium Hypochlorite Solutions

1. Butyraldehyde Removal

Data: From Table 5-5

Gas: Flow rate: 20 cfm
Inlet odor conc., y_E : 236.4×10^{-6}
Outlet odor conc., y : 101.3×10^{-6}
Liquid: Flow rate: 1.0 gpm
NaOCl conc.: 0.117g/100 ml
pH: 11.1

Calculations:

Mass flux:

$$G = 450 \text{ lb}/(\text{ft}^2)(\text{hr})$$

$$L = 2500 \text{ lb}/(\text{ft}^2)(\text{hr})$$

Molar flux:

$$G_m = 15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

$$L_m = 138.9 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

Henry's law constant:

From Tables 3-1 and 5-1

$$h_{\text{Na}^+} = -0.0183; \quad h_{\text{OCl}^-} = 0.3497$$

$$h_{\text{OH}^-} = 0.3875; \quad h_g = -0.1716$$

$$h_{\text{NaOCl}} = -0.0183 + 0.3497 - 0.1716 = 0.1589 \quad (\text{Equation 3-5})$$

$$h_{\text{NaOH}} = -0.0183 + 0.3875 - 0.1716 = 0.1976 \quad (\text{Equation 3-5})$$

$$C_{\text{NaOCl}} = (0.117 \text{ g}/100 \text{ ml})/(74.5 \text{ g/gmole}) = 0.0157 \text{ gmole/l}$$

$$C_{\text{NaOH}} = 0.001 \text{ gmole/l}$$

$$I_{\text{NaOCl}} = \frac{1}{2}(0.0157 + 0.0157) = 0.0157$$

$$I_{\text{NaOH}} = \frac{1}{2}(0.001 + 0.001) = 0.001$$

$$\text{From Figure 5-1, } H_e^\circ = 9.64$$

From Equation 3-6

$$\log(H_e/H_e^\circ) = (0.1598)(0.0157) + (0.1976)(0.001) = 0.0045$$

$$H_e = 1.01 H_e^\circ = 9.74$$

Overall gas-side mass transfer coefficient:

Because the oxidation of butyraldehyde by sodium hypochlorite is a very slow reaction, Equation 3-18 and 3-19 were used

$$S = \frac{(9.74)(15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr}))}{138.9 \text{ lb mole}/(\text{ft}^2)(\text{hr})} = 1.087$$

$$K_{Ga} = \frac{15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{(2.8 \text{ ft})(1 - 1.087)} \ln((1 - 1.087) \left(\frac{236.7 \times 10^{-6}}{101.3 \times 10^{-6}} \right) + 1.087) = 7.71 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Liquid-side mass transfer coefficient:

The gas-side mass transfer resistance is negligible, so Equation 3-10 becomes

$$\begin{aligned} k_{La} &= (H_e)(K_{Ga}) = (9.74)(7.71 \text{ lb mole}/(\text{ft}^3)(\text{hr})) \\ &= 75.1 \text{ lb mole}/(\text{ft}^3)(\text{hr}) \end{aligned}$$

Enhancement factor:

$$\text{Reading Table 5-4, } (k_{La})_{\text{phys.}} = 47.5 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

From Equation 3-33

$$\phi = \frac{75.1 \text{ lb mole}/(\text{ft}^3)(\text{hr})}{47.5 \text{ lb mole}/(\text{ft}^3)(\text{hr})} = 1.55$$

2. n-Butyl Mercaptan Removal

Data: From Table 5-6

Gas: Flow rate: 20 cfm
Inlet odor conc., y_B : 223.5×10^{-6}
Outlet odor conc., y_T : 11.5×10^{-6}
Liquid: Flow rate: 0.5 gpm
NaOCl conc.: 0.104 g/100 ml
pH: 10.6

Calculations:

Mass flux:

$$G = 450 \text{ lb}/(\text{ft}^2)(\text{hr})$$

$$L = 1250 \text{ lb}/(\text{ft}^2)(\text{hr})$$

Molar flux:

$$G_m = 15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

$$L_m = 69.4 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

Henry's law constant:

From Table 3-1 and 5-1

$$h_g = -0.0761; \quad h_{\text{OCl}^-} = 0.3497$$

$$h_{\text{Na}^+} = -0.0183; \quad h_{\text{OH}^-} = 0.3875$$

$$h_{\text{NaOCl}} = -0.0183 + 0.3497 - 0.0761 = 0.2553 \text{ (Equation 3-5)}$$

$$h_{\text{NaOH}} = -0.0183 + 0.3875 - 0.0761 = 0.2931 \text{ (Equation 3-5)}$$

$$C_{\text{NaOCl}} = (0.104 \text{ g}/100 \text{ ml})/(74.5 \text{ g/gmole}) = 0.014 \text{ gmole/l}$$

$$C_{\text{NaOH}} = 10^{10.6-14} = 0.00025 \text{ gmole/l}$$

$$I_{\text{NaOCl}} = \frac{1}{2}(0.014 + 0.014) = 0.014$$

$$I_{\text{NaOH}} = \frac{1}{2}(0.00025 + 0.00025) = 0.00025$$

From Table 5-2, $H_e^\circ = 120$

From Equation 3-6

$$\log(H_e/H_e^\circ) = (0.2553)(0.014) + (0.2931)(0.00025) = 0.0036$$

$$H_e = 1.008 H_e^\circ = 121$$

Overall gas-side mass transfer coefficient:

Because the reaction occurring in the scrubbing system is a fast one, the overall gas-side mass transfer coefficient can be determined from Equation 3-29 in terms of

$$K_{Ga} = \frac{15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{2.8 \text{ ft}} \ln \left(\frac{223.5 \times 10^{-6}}{11.5 \times 10^{-6}} \right)$$
$$= 16.4 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Liquid-side mass transfer coefficient:

Since the gas-side mass transfer resistance is negligible,

Equation 3-10 becomes

$$k_{La} = (H_e)(K_{Ga}) = (121)(16.4 \text{ lb mole}/(\text{ft}^3)(\text{hr}))$$
$$= 1984 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Enhancement factor:

Reading Table 5-4

$$(k_{La})_{\text{phys.}} = 36.0 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

From Equation 3-33

$$\phi = \frac{1984 \text{ lb mole}/(\text{ft}^3)(\text{hr})}{36.0 \text{ lb mole}/(\text{ft}^3)(\text{hr})} = 55.1$$

C. Wet Scrubbing With Alkaline Potassium Permanganate Solutions

1. Butyraldehyde Removal

Data: From Table 5-7

Gas: Flow rate: 20 cfm
Inlet odor conc., y_B : 229.1×10^{-6}
Outlet odor conc., y_T : 37.3×10^{-6}
Liquid: Flow rate: 1.0 gpm
 KMnO_4 conc.: 0.2 g/100 ml
pH: 11.0

Calculations:

Mass flux:

$$G = 450 \text{ lb}/(\text{ft}^2)(\text{hr})$$

$$L = 2500 \text{ lb}/(\text{ft}^2)(\text{hr})$$

Molar flux:

$$G_m = 15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

$$L_m = 138.9 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

Henry's law constant:

From Tables 3-1 and 5-1

$$h_{K^+} = -0.0362; \quad h_{\text{MnO}_4^-} = 0.3321; \quad h_g = -0.1716$$

$$h_{\text{Na}^+} = -0.0183; \quad h_{\text{OH}^-} = 0.3875$$

$$h_{\text{KMnO}_4} = -0.0362 + 0.3321 - 0.1716 = 0.1243 \text{ (Equation 3-5)}$$

$$h_{\text{NaOH}} = -0.0183 + 0.3875 - 0.1716 = 0.1975 \text{ (Equation 3-5)}$$

$$C_{\text{KMnO}_4} = (0.2 \text{ g}/100\text{ml})/(158 \text{ g/gmole}) = 0.013 \text{ gmole/l}$$

$$C_{\text{NaOH}} = 0.001 \text{ gmole/l}$$

$$I_{KMnO_4} = \frac{1}{2}(0.013 + 0.013) = 0.013$$

$$I_{NaOH} = \frac{1}{2}(0.001 + 0.001) = 0.001$$

From Figure 5-2, $H_e^\circ = 9.64$

From Equation 3-6

$$\log(H_e/H_e^\circ) = (0.1243)(0.013) + (0.1975)(0.001) = 0.0018$$

$$H_e = 1.004 H_e^\circ = 9.68$$

Overall gas-side mass transfer coefficient:

The oxidation of butyraldehyde by permanganate is very slow and can be neglected. Therefore, Equations 3-18 and 3-19 were employed

$$S = \frac{(9.68)(15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr}))}{138.9 \text{ lb mole}/(\text{ft}^2)(\text{hr})} = 1.08$$

$$K_{Ga} = \frac{15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{(2.8 \text{ ft})(1 - 1.08)} \ln\left((1 - 1.08)\left(\frac{229.1 \times 10^{-6}}{87.3 \times 10^{-6}}\right) + 1.08\right) = 9.6 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Liquid-side mass transfer coefficient:

Neglecting the gas-side mass transfer resistance, Equation 3-10 gives

$$\begin{aligned} k_{La} &= (H_e)(K_{Ga}) = (9.68)(9.6 \text{ lb mole}/(\text{ft}^3)(\text{hr})) \\ &= 93.2 \text{ lb mole}/(\text{ft}^3)(\text{hr}) \end{aligned}$$

Enhancement factor:

$$\text{Reading Table 5-4, } (k_{La})_{\text{phys.}} = 47.5 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

From Equation 3-33

$$\phi = \frac{93.2 \text{ lb mole}/(\text{ft}^3)(\text{hr})}{47.5 \text{ lb mole}/(\text{ft}^3)(\text{hr})} = 1.96$$

2. n-Butyl Mercaptan Removal

Data: From Table 5-3

Gas: Flow rate: 20 cfm
Inlet odor conc., y_B : 174×10^{-6}
Outlet odor conc., y_T : 12×10^{-6}
Liquid: Flow rate: 0.5 gpm
 KMnO_4 conc.: 0.2 g/100 ml
pH: 11.1

Calculations:

Mass flux:

$$G = 450 \text{ lb}/(\text{ft}^2)(\text{hr})$$

$$L = 1250 \text{ lb}/(\text{ft}^2)(\text{hr})$$

Molar flux:

$$G_m = 15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

$$L_m = 69.4 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

Henry's law constant:

From Table 3-1 and 5-1

$$h_{K^+} = -0.0362; \quad h_{\text{MnO}_4^-} = 0.3321; \quad h_g = -0.0761$$

$$h_{\text{Na}^+} = -0.0183; \quad h_{\text{OH}^-} = 0.3875$$

$$h_{\text{KMnO}_4} = -0.0362 + 0.3321 - 0.0761 = 0.2198 \text{ (Equation 3-5)}$$

$$h_{\text{NaOH}} = -0.0183 + 0.3875 - 0.0761 = 0.2752 \text{ (Equation 3-5)}$$

$$C_{\text{KMnO}_4} = (0.2 \text{ g}/100 \text{ ml})/(158 \text{ g/gmole}) = 0.013 \text{ gmole/l}$$

$$C_{\text{NaOH}} = 0.001 \text{ gmole/l}$$

$$I_{\text{KMnO}_4} = \frac{1}{2}(0.013 + 0.013) = 0.013$$

$$I_{\text{NaOH}} = \frac{1}{2}(0.001 + 0.001) = 0.001$$

From Figure 5-2, $H_e^o = 120$

From Equation 3-6

$$\log(H_e/H_e^o) = (0.2198)(0.013) + (0.2752)(0.001) = 0.003$$

$$H_e = 1.007 H_e^o = 120.8$$

Overall gas-side mass transfer coefficient:

The reaction occurring in the scrubbing process is fast. From Equation 3-29

$$K_{Ga} = \frac{15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{2.8 \text{ ft}} \ln\left(\frac{174 \times 10^{-6}}{12 \times 10^{-6}}\right) \\ = 14.8 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Liquid-side mass transfer coefficient:

Neglecting the gas-side mass transfer resistance, Equation 3-10 yields

$$k_{La} = (H_e)(K_{Ga}) = (120.8)(14.8 \text{ lb mole}/(\text{ft}^3)(\text{hr})) \\ = 1788 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Enhancement factor:

Reading Table 5-4

$$(k_{La})_{\text{phys.}} = 36.0 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

From Equation 3-33

$$\phi = \frac{1788 \text{ lb mole}/(\text{ft}^3)(\text{hr})}{36.0 \text{ lb mole}/(\text{ft}^3)(\text{hr})} = 49.7$$

APPENDIX V

Application of Mass Transfer Data to Wet Scrubber Design

The examples presented here demonstrate the application of experimental data to packed bed scrubber design. Units are to meet conditions established by

- i. types and compositions of liquids and gases at inlet and outlet;
- ii. liquid and gas flow rates;
- iii. packing type, material and size;
- iv. column diameter.

Example 1.

About 22,500 lb/hr of effluent gas from an industrial plant, containing 500 ppm butyraldehyde, is to be treated with 125,000 lb/hr of 0.03 wt% KMnO_4 solution at pH 12 (adjusted with NaOH). A packed tower operating at 25°C and atmospheric pressure is to be designed to reduce the composition of butyraldehyde to 50 ppm. If the diameter of the scrubber is to be 8 ft and 5/8 in. stainless steel Pall rings are chosen in this design, what height is required to handle this amount of gas.

Design calculations:

$$\text{Cross sectional area of scrubber} = (\pi)(8 \text{ ft})^2/4 = 50 \text{ ft}^2$$

Mass flux:

$$G = \frac{22,500 \text{ lb/hr}}{50 \text{ ft}^2} = 450 \text{ lb/}(\text{ft}^2)(\text{hr})$$

$$L = \frac{125,000 \text{ lb/hr}}{50 \text{ ft}^2} = 2,500 \text{ lb/}(\text{ft}^2)(\text{hr})$$

Molar flux:

$$G_m = \frac{450 \text{ lb}/(\text{ft}^2)(\text{hr})}{29 \text{ lb/lb mole}} = 15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

$$L_m = \frac{2,500 \text{ lb}/(\text{ft}^2)(\text{hr})}{18 \text{ lb/lb mole}} = 138.9 \text{ lb mole}/(\text{ft}^2)(\text{hr})$$

Liquid-side mass transfer coefficient:

The physical liquid-side mass transfer coefficient at $L = 2,500 \text{ lb}/(\text{ft}^2)(\text{hr})$ is obtained from Table 5-4

$$(k_L a)_{\text{phys.}} = 47.5 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

The enhancement factor for 0.03 wt% KMnO_4 solution at pH 12 can be read from Figure 5-12 as

$$\phi = 1.94$$

From Equation 3-33

$$\begin{aligned} (k_L a)_{\text{chem.}} &= (\phi)(k_L a)_{\text{phys.}} = (1.94)(47.5 \text{ lb mole}/(\text{ft}^3)(\text{hr})) \\ &= 92.15 \text{ lb mole}/(\text{ft}^3)(\text{hr}) \end{aligned}$$

Henry's law constant:

From Tables 3-1 and 5-1

$$h_{\text{K}^+} = -0.0362; \quad h_{\text{MnO}_4^-} = 0.3321; \quad h_g = -0.1716$$

$$h_{\text{Na}^+} = -0.0183; \quad h_{\text{OH}^-} = 0.3875$$

$$h_{\text{KMnO}_4} = -0.0362 + 0.3321 - 0.1716 = 0.1243 \text{ (Equation 3-5)}$$

$$h_{\text{NaOH}} = -0.0183 + 0.3875 - 0.1716 = 0.1975 \text{ (Equation 3-5)}$$

$$C_{\text{KMnO}_4} = (0.03 \text{ g}/100 \text{ ml})/(158 \text{ g/gmole}) = 0.0019 \text{ gmole/l}$$

$$C_{\text{NaOH}} = 0.01 \text{ gmole/l}$$

$$I_{\text{KMnO}_4} = \frac{1}{2}(0.0019 + 0.0019) = 0.0019$$

$$I_{\text{NaOH}} = \frac{1}{2}(0.01 + 0.01) = 0.01$$

From Figure 5-1

$$H_e^o = 9.64$$

The Henry's law constant in solution is estimated from Equation 3-6

$$\log(H_e/9.64) = (0.1243)(0.0019) + (0.1975)(0.01) = 0.0022$$

$$H_e = 1.005 * 9.64 = 9.69$$

Overall gas-side mass transfer coefficient:

By neglecting the gas-side mass transfer resistance, the overall gas-side mass transfer coefficient can be calculated from Equation 3-10

$$K_{Ga} = \frac{92.15 \text{ lb mole}/(\text{ft}^3)(\text{hr})}{9.69} = 9.5 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Height of packed bed:

The oxidation of butyraldehyde by alkaline KMnO_4 solution is very slow and can be considered negligible, therefore Equation 3-18 and 3-19 are applicable

$$S = \frac{9.69 * 15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{138.9 \text{ lb mole}/(\text{ft}^2)(\text{hr})} = 1.081$$

$$Z = \frac{15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{(9.5 \text{ lb mole}/(\text{ft}^3)(\text{hr}))(1-1.081)} \ln((1 - 1.081))$$
$$\left(\frac{500 * 10^{-6}}{50 * 10^{-6}} \right) + 1.081 = 26 \text{ ft}$$

Example 2.

In a refining plant, absorption of n-butyl mercaptan with alkaline sodium hypochlorite is being considered. The gas flow rate from the plant to the scrubber is 22,500 lb/hr. This gas stream contains 1000 ppm n-butyl mercaptan. The amount of n-butyl mercaptan in the exit gas must be lowered to 2 ppm. The liquid feed to the scrubber will be 62,500 lb/hr of 0.01 wt% NaOCl solution at pH 12. What height of a 8 ft tower packed with 5/8 in stainless steel Pall rings is required. The operating conditions for this scrubbing system are 1 atm and about 25° C.

Design calculations:

$$\text{Cross sectional area of scrubber} = (\pi)(8 \text{ ft})^2/4 = 50 \text{ ft}^2$$

Mass flux:

$$G = \frac{22,500 \text{ lb/hr}}{50 \text{ ft}^2} = 450 \text{ lb/ft}^2(\text{hr})$$

$$L = \frac{62,500 \text{ lb/hr}}{50 \text{ ft}^2} = 1250 \text{ lb/ft}^2(\text{hr})$$

Molar flux:

$$G_m = \frac{450 \text{ lb/ft}^2(\text{hr})}{29 \text{ lb/lb mole}} = 15.5 \text{ lb mole/ft}^2(\text{hr})$$

$$L_m = \frac{1250 \text{ lb/ft}^2(\text{hr})}{18 \text{ lb/lb mole}} = 69.4 \text{ lb mole/ft}^2(\text{hr})$$

Liquid-side mass transfer coefficient:

From Table 5-4, at $L = 1250 \text{ lb}/(\text{ft}^2)(\text{hr})$

$$(k_L a)_{\text{phys.}} = 36.0 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

The enhancement factor for 0.01 wt% NaOCl solution at pH 12 is obtained from Figure 5-10 as

$$\phi = 45.1$$

The liquid-side mass transfer coefficient is obtained from Equation 3-33 as

$$\begin{aligned}(k_L a)_{\text{chem.}} &= (\phi)(k_L a)_{\text{phys.}} = (45.1)(36.0 \text{ lb mole}/(\text{ft}^3)(\text{hr})) \\ &= 1623.6 \text{ lb mole}/(\text{ft}^3)(\text{hr})\end{aligned}$$

Henry's law constant:

From Tables 3-1 and 5-1

$$h_{\text{Na}^+} = -0.0183; \quad h_{\text{OCl}^-} = 0.3497$$

$$h_{\text{OH}^-} = 0.3875; \quad h_g = -0.0761$$

$$h_{\text{NaOCl}} = -0.0183 + 0.3497 - 0.0761 = 0.2553 \text{ (Equation 3-5)}$$

$$h_{\text{NaOH}} = -0.0183 + 0.3875 - 0.0761 = 0.2931 \text{ (Equation 3-5)}$$

$$C_{\text{NaOCl}} = (0.01 \text{ g}/100 \text{ ml})/(74.5 \text{ g/gmole}) = 0.0013 \text{ gmole/l}$$

$$C_{\text{NaOH}} = 0.01 \text{ gmole/l.}$$

$$I_{\text{NaOCl}} = \frac{1}{2}(0.0013 + 0.0013) = 0.0013$$

$$I_{\text{NaOH}} = \frac{1}{2}(0.01 + 0.01) = 0.01$$

From Figure 5-2

$$H_e^\circ = 120$$

The Henry's law constant can be calculated from Equation 3-6

$$\log(H_e/H_e^\circ) = (0.2553)(0.0013) + (0.2931)(0.01) = 0.0033$$

$$H_e = 1.007 H_e^\circ = 121$$

Overall gas-side mass transfer coefficient:

For system in which the gas-side mass transfer resistance is negligible, Equation 3-10 yields

$$K_{Ga} = \frac{k_g a}{H_e} = \frac{1623.6 \text{ lb mole}/(\text{ft}^3)(\text{hr})}{121}$$

$$= 13.4 \text{ lb mole}/(\text{ft}^3)(\text{hr})$$

Height of packed bed:

Because a fast reaction occurs when n-butyl mercaptan dissolves into alkaline sodium hypochlorite solution, Equation 3-29 must be used to give

$$Z = \frac{15.5 \text{ lb mole}/(\text{ft}^2)(\text{hr})}{13.4 \text{ lb mole}/(\text{ft}^3)(\text{hr})} \ln\left(\frac{1000 \times 10^{-6}}{2 \times 10^{-6}}\right)$$

$$= 7.2 \text{ ft}$$

VITA

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